

## PREPARATION THEREOF

### OXYGEN-CONTAINING ALUMINUM COMPOUND AND METHOD OF PREPARATION THEREOF

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Inventor(s):  
KACHKIN A V;; MAKARENKO M G;; BORISOVA T V;; SOTNIKOV V V

Applicant(s):  
KATALIZATOR AOOT

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#### Abstract

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FIELD: industrial inorganic synthesis. SUBSTANCE: invention relates to production of different modifications of aluminum oxide and aluminum hydroxide used as fillers and absorbents and also as starting material for production of aluminum salts, etc. According to invention, oxygen-containing aluminum compound of general formula  $Al_2O_3 \cdot nH_2O$  prepared by rapid partial dehydration of aluminum hydroxide and containing Al(III) cations in 4,5,6-coordination state with respect to oxygen additionally contains at least one compound of element selected from group including: Na, K, Si, B, C, Ti, Zr, Ba, Ca, Mg, Ga, Sn, and La in amounts 0.01 to 2.0 wt.% (on conversion to oxides) with value of  $n = 0.03$  to 2.0 and having specific surface from 50 to 450 sq.m/g. The obtained oxygen-containing compound has amorphous or poorly crystallized structure or partially crystalline structure. Method of preparing such compound involves rapid partial high-

temperature (300- 1200 C) dehydration of aluminum oxide additionally containing at least one compound of the above-listed elements followed by hardening at temperature no higher than 280 C to form final compound with formula  $Al_2O_3 \cdot nH_2O$  wherein  $n=0.3-2.0$ . EFFECT: enabled preparation of aluminum compound with a variety of physico-chemical properties including catalysts for a series of processes. 4 cl, 1 tbl, 16 ex

## MATERIAL AND METHOD FOR COATING GLASS FORMING EQUIPMENT FIELD OF THE INVENTION

The present invention relates to protective coatings for surfaces of glass forming equipment and methods of applying the same thereto, and more particularly to protective coatings for, and methods of applying such coatings to, plungers for forming glass articles, to replace chrome coatings customarily utilized for coating such plungers.

## BACKGROUND OF THE INVENTION

Chrome plating has been used on glass forming equipment for more than 40 years. Its primary function has been to provide oxidation and corrosion protection to the forming equipment substrate material. Generally the base material utilized in glass forming equipment may be either 420 stainless steel, H13 tool steel or ductile iron, depending upon the application. Although chromium plating of glass forming equipment has been utilized successfully over many years with different glass compositions, serious problems are encountered when the desired product requires a glass composition containing significant amounts of alkali and/or alkaline components.

A problem results which is defined as the build-up of a corrosion product on the surface of the chromium plated forming equipment, which results in unacceptable glass matte surface.

The corrosion product is the result of a reaction involving the alkali and alkaline components of the glass, oxygen, and chromium from the chrome plated forming equipment. The reaction products have been identified as chromate compounds, namely  $K_3Na(CrO_4)_2$ ,  $BaK_2(CrO_4)_2$  and  $K_3Ba_2Cr_3O_{13}$ . If any one of the three reactants, glass components, the oxygen, or the chrome from the chromeplated forming equipment were removed from the system, the chromate corrosion problem would cease to exist. In view of the fact that the glass composition is usually dictated by the desired end product, and oxygen is in the atmosphere, it becomes obvious that the most practical solution to the problem is to eliminate the chrome plated forming equipment.

From a pure production standpoint, the need to find a replacement for chrome electroplating of forming equipment, is based upon improved performance of the equipment, however environmental issues also adds impetus to the need for change from the use of chrome plating, since there is a need to reduce the environmental risks associated with chrome-electroplating. That is, there is a global trend of hexavalent chrome emission reduction, and the substituted coating materials of the present invention help to reduce such hexavalent chrome emissions.

The chromate corrosion product does not contaminate the glass per se, but accumulates on the chrome-plated glass forming surface and necessitates the replacement thereof in order to produce acceptable ware. In U. S.

Patent No. 5,120,341 to Nozawa et al., the inventors desire to increase the strength of glass containers by decreasing contaminants actually getting into the glass.

In order to reduce glass contamination, the patent suggests the use of a gaseous hydrocarbon to coat the mold parts instead of using oil, which creates bubbles and graphite contamination of the glass. In addition, the patent suggests the coating of a plunger with a ceramic or sprayed metal coating which prevents flaking of an oxide layer from the plunger into the glass. Since the ceramic coating can withstand higher temperatures than the metal coating, the patent suggests coating the tip of the plunger with the ceramic coat and the base of the plunger with a self-fluxing metal coating, which cannot withstand the higher temperatures to which the tip of the plunger is exposed.

Further, the sprayed metal coating is less abrasive than the ceramic coating and thus is utilized at the base of the plunger so as to not scratch the glass container about the mouth portion. In another embodiment, the patent suggests the use of a blown air curtain about the plunger which not only cools the plunger but is used mainly in order to prevent foreign substances from attaching to the outside surface of the plunger, which foreign substances would contaminate the newly formed glass. Finally, the patent also suggests the use of an abrasive proof layer between the moving surfaces of the plunger assembly to prevent metal dusts from contaminating the glass, which dust particles would decrease the impact strength of the formed glass container. Unlike the Nozawa et al. Patent, the present invention is not concerned with the contamination of the glass per se, but with the provision of a protective coating to protect substrate material of glass forming equipment, such as a plunger, from oxidation and corrosion.

However, in U. S. Patent No. 4,830,655 to Franek et al., the inventors were looking for a material to avoid the chemical incompatibilities of known mold materials and glass melts in the forming of glass optical elements with high surface quality. The mold means of the Franek et al.

Patent must have a monocrystalline structure and is made from material such as A1203, Cr2O3 (which is being avoided in the present invention), MgAl2O4 and/or ZrO2. The shaping device itself is prepared by means of chip forming shaping processes (for example boring, sawing, turning, milling, etc.), from a solid piece of material with subsequent final processing of the mold surfaces (honing, polishing, burnishing, glazing, buffing, etc.). Thus, it can be seen that the Franek et al. Patent does not even contemplate the utilization of a coating applied to a substrate, but actually manufactures the shaping device from a block of material having a monocrystalline structure.

Again, unlike the Franek et al. Patent which forms its shaping device from a solid piece of material by machining the material, the present invention applies a protective coating to additional substrate material for forming glass articles. Thus it has been an object of the invention to not only avoid the utilization of chrome as a plating material, but also to provide an improved corrosion and oxidation resistant coating for glass forming equipment.

#### SUMMARY OF THE INVENTION

The present invention sets forth corrosion and oxidation resistant coatings and methods of applying the same to glass forming equipment to replace the use of chrome as a plating material on such equipment. Coating materials such as A12O3, and Ni/V may be utilized and an undercoat of Ni or nickel alloy may be employed. The method of deposition onto the substrate of the forming equipment may include sputter coating and electron beam physical vapor deposition.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The criteria for material selection was based primarily upon the assumed compatibility of a material with the hot glass forming environment, specifically high temperature oxidation and corrosion resistance. Other factors such as material toxicity and availability were also considered. Initially 28 materials were selected to be deposited upon test samples in order to have a broad base from which to select the most optimum coating material.

However, since the problem of the build-up of a corrosion product manifests itself primarily on plunger surfaces utilized to form TV panels, it was important to design a test to model the production pressing process and simulate actual conditions for life and performance predictions

specific to such problem. Therefore, specifically designated coated samples were cyclicly immersed in TV panel glass under controlled conditions at elevated temperatures. The controlled test conditions were glass temperature, plunger temperature, dwell (immersion) time, cycle time and test duration.

Since the initial test for the 28 selected materials was designed to simulate production process conditions, the glass temperature was maintained at 1000 C with the plunger surface temperature controlled at 600 C. Automatic temperature control of the plunger was accomplished by blowing cooling-air on the backside of the test plungers.

A thermocouple linked to a pneumatically controlled valve regulated the amount of cooling air applied to the plunger. The initial control set was determined with the aid of a contact pyrometer in the plunger up position.

The plunger and glass temperatures were collected throughout the test periods. At the end of each test the data was plotted to verify that stable conditions existed throughout the duration of the test.

Dwell and cycle times were set at 12 seconds and 4 cuts/minute, respectively. These times were based on the pressing of a 27 inch TV panel. In the down, or dwell position, the coated plunger was immersed in hot glass contained in a crucible inside an electric box furnace.

When the dwell time cycle was reached, the plunger was retracted up and out of the glass through a hole in the furnace lid, stopping approximately 11 inches above the furnace. Test duration was standardized at 48 hours.

The test plungers were made of 420 stainless steel to represent the substrate material commonly used for plungers. A blind hole was machined into the backside of the plunger for insertion of a thermocouple to control plunger temperature. Further, a design incorporating a high temperature gasket and seating flange was used to prevent cooling air from escaping from the furnace chamber, since it was felt that excess oxygen at the coating/glass interface would skew test results. The test plungers were polished and stippled as per the standard production process.

The following is a list of the 28 materials which were deposited upon the test plunger samples and the deposition process utilized.

#### Material Deposition Process

Cr Electroplate Cr2O3 Plasma Spray Coat

Cr2O3Si Plasma Spray Coat

CrN/CrC Physical Vapor Deposition

TiC Physical Vapor Deposition TiCN Physical Vapor Deposition

TiAlN Physical Vapor Deposition TiC/Al2O3 Chemical Vapor Deposition

TiN Physical Vapor Deposition

TiCN/TiC/TiCN/TiN Chemical Vapor Deposition

MCrAlY Physical Vapor Deposition

Dura-Nickel 301 Physical Vapor Deposition

Stellite 6 Physical Vapor Deposition MgO Physical Vapor Deposition Ni/N Sputter Coating

Al2O3 Physical Vapor Deposition

Nb/NbC Physical Vapor Deposition B4C/W Physical Vapor Deposition B4C/MO Physical Vapor Deposition SiC/W Physical Vapor Deposition SiC/MO Physical Vapor Deposition

ZrO2 Physical Vapor Deposition

CoCrAlY Physical Vapor Deposition

Pt/Rh Physical Vapor Deposition

Ir Physical Vapor Deposition ErO Physical Vapor Deposition

TiB2 Physical Vapor Deposition NiWB Electroplate

A target deposition thickness range of about 5-10 pm was targeted, based upon the need for

adequate protection from wear and to insure oxidation/corrosion protection of the 420 SS substrate material. It was felt that too thin of a coating may not hold up to the abrasive wear encountered in the production forming process over the course of long runs. Conversely, if the coating was too thick, detrimental residual tensile stresses could buildup in the deposition initiating cracks, which offer a pathway to the unprotected substrate.

After comparing the attributes of the major families of deposition processes, as they relate to the present invention, it was decided that physical vapor deposition (PVD) was best suited to meet present requirements.

Chemical vapor deposition (CVD), while offering dense, well adhered depositions, requires process temperatures in excess of the base metals upper limit of 600 C. Processing above this temperature would negatively impact the mechanical properties of the 420 SS substrate as well as raise the risk of dimensional distortion.

The state of the art in spray coating technology, in terms of density and microstructure homogeneity has not advanced to the point of being useable for TV panel forming equipment applications. Plasma spray coating does not produce acceptable densities or uniformity. Another shortcoming of the spray coating technology is the need for additional finishing steps once the deposition has been completed. Electroplating is a proven technology in the glass forming industry, however, it is relatively inflexible in terms of coating materials options. The two greatest detriments associated with electroplating, however, are the environmental risks and the cost of compliance. The PVD process, especially electron beam PVD (EB-PVD) appears to satisfy several important criteria, which is further enhanced with ion beam assisted deposition (IBAD). The EB-PVD with IBAD is preferred since it has the capability of producing dense, tightly adhered coatings, with acceptable deposition rates and under controllable conditions without environment risk.

The coatings were examined for adherence, oxide formation, pitting or other indications of corrosion.

Surface roughness, which was hoped to have been a key quantitative measure, displayed no correlation with performance. The most common reason for failure was poor oxidation resistance, poor in relative terms meaning that oxidation resistance was not equal to chrome electroplate.

The focus of the invention has been to identify and apply materials that display the potential to exceed the performance of chrome electroplate.

Upon reviewing the results of the tests of the 28 materials deposited on the test plungers, it was determined that both A1203 and MgO looked exceptional after 48 hours testing. All of the coatings were deposited via the PVD process without a bond coat, with the A1203 and MgO being deposited by the electron beam physical vapor deposition process whereas the Ni/V was deposited by a sputtered physical vapor deposition process. Although the differences in coefficient of thermal expansion of MgO and A1203 with 420 SS slightly favors MgO, A1203 was favored based on the overall appearance of the two coatings, and the lower likelihood of sublimation with A1203. Further, it may be desirable to use a bond coat to match expansion coefficients between the A1203 and the 420 SS, such as Ni or a nickel alloy such as CoNiCrAlY, which can be applied during the same EB-PVD process that applies the A1203.

#### Example 1.

A standard plunger for forming TV panels was given a standard automatic stipple process, the stipple machine rinsed the plunger at the end of the cycle, with no other cleaning or rinsing performed on the part. The standard stipple process was set to hit a target of 30 Ra surface roughness, with subsequent plating and bead blasting yielding a finish roughness of approximately 20 Ra. The plunger was bolted to a platen and positioned face-up and rolled into a

vacuum chamber. Once in the chamber the platen was rotated to give the plunger a 30 disposition angle relative to the target source. After the chamber was pumped down to  $2 \times 10^{-7}$  Torr, the plunger was glow discharge cleaned with the ion beam source for 15 minutes.

The set up included a container of target material, an ion beam source, an electron beam source, a substrate holder positioned relative to the target source, and a rotational shaft to rotate the substrate holder.

Process Set-Up:

Target material 99.99% pure aluminum oxide,  
manufactured by Cerac, 1.5-3  
mm size  
Base pressure 2 Torr  
Deposition pressure 02 partial pressure  $4 \times 10^{-5}$   
Torr  
Ar partial pressure  $2 \times 10^{-5}$   
Torr  
Electron beam gun Voltage-8 Killowatts  
Curent- 1 Ampere  
Ion beam source Endhall  
Ion oxygen channel Oxygen flow rate-120 sccm  
Anode voltage-167 volts  
Curent-3.2 amperes  
Ion Argon channel Argon flow rate-15.2 sccm  
Anode voltage-18.3 volts  
Curent-3.41 amperes  
Deposition angle 30 degrees  
Substrate RPM. 5  
Substrate temperature Approximately 100 C.

Deposition rate Approximately 10A/sec.

Evaluation of dimensional measurements on several panels showed that contour variation was not more than normal, indicating positive results. Also, based on the results from the coating trial, aluminum oxide appeared to have more lubricity than chrome plating, thus minimizing the potential frequency to lubricate the plunger. The aluminum oxide coating of about 4  $\mu\text{m}$  showed no measurable loss in thickness caused by scrubbing, which is due to the very high abrasive wear resistance of A1203, as compared with chrome plating. The A1203 coating appeared to be firmly attached to the substrate, and as expected no yellow chromate was found on the plunger.

A scanning electron microscope was utilized to determine the thickness measurements of the coating on the plunger, and it was found that the coating thickness was greater in the center face and radius areas. In order to increase the thickness of the coating on the corners of the plungers, it was felt that this could be accomplished by changing the tilt angle and pausing the rotation of the substrate to concentrate the condensing vapors at each corner. The SEM analysis indicated that the overall coating was of good quality, the grain structure was columnar, and appeared dense and tightly adhered to the plunger. However, since alumina is very brittle, and there is an expansion coefficient mismatch between the alumina and the stainless steel, some microcracking was expected, and even though minimal microcracking was observed in the alumina it was sufficient for enough oxygen to reach the substrate to oxidize the iron. The problem of expansion coefficient mismatch can be easily corrected by depositing a thin (1-2 microns) oxidation resistant coating layer under the alumina, such as a layer of nickel or nickel alloy. This is easily accomplished by indexing a crucible of nickel target material under the electron gun during the coating process.

Example 2

A stainless steel plunger for forming 27 inch TV panels was coated with aluminum oxide and utilized to press TV panels to test the efficiency of the aluminum oxide coating. The coating was applied in accordance with the following process.

#### Deposition Process

Plunger was processed prior to coating according to the following process: 1. Standard polish 2. Standard stipple 3. Standard glass beading 4. De-ionized water rinse 5. Methanol rinse 6. Air hose dry off

#### Coating Parameters

Base pressure:  $2.8 \times 10^{-7}$  Torr

R. P. M.: 3 throughout 1. Cleaning Process: Start 10: 22 AM; Finish 10: 37 AM

RF ion source with Argon

RF power 400 watts

Beam current 440 watts

Suppressor 1040 volts

Accelerator 990 volts

Gas 91 sccm Ar System pressure  $8.7 \times 10^{-5}$  Torr 2. First coating process: Start 11: 03 AM; Finish 1: 55 PM

#### Initial Conditions:

Ion beam:

RF source with Oxygen

RF Power 400 watts

Beam current 200 watts

Suppressor 518 volts Gas 99.9 sccm 2

Deposition angle-initially @ 25 then changed to 35 after six minutes

Electron beam gun # 1 (large hearth):

Beam voltage 8000 volts

Beam current 0.7 amps

Controller power 81%

Rate 5.1 A/sec

Thickness 0

System pressure  $2.11 \times 10^{-5}$  Torr

#### Final Conditions:

Ion beam:

RF ion source with Oxygen

RF power 403 watts

Beam current 273 watts

Suppressor 518 volts

Accelerator 912 volts

Gas 102.9 sccm System pressure  $1.46 \times 10^{-5}$  Torr

Electron beam gun #1 (large hearth):

Beam voltage 8,500 volts

Beam current 0.8 amps

Controller power 85%

Rate 6.2 A/sec

Thickness 63,800 A (at crystal)

As a sub experiment the coating thickness in corners at the ends of one side of the plunger and designated as "A" & "D" was increased. This was done to test the theory that oxidation resistance in the corners could be improved with increased coating thickness, and was accomplished by halting the plunger rotation when corner "A" was nearest the target & held until 2,000 A was deposited. Corner "D" was then rotated into position and the process was duplicated. This process was repeated four more times to give a total of 10,000 A of additional coating thickness to each corner.

To test the lubricity of the coating, the sidewall between corners "A" & "D" and an adjacent sidewall

were not prepped with Moly-di-Sulfide.

After the run of pressing several hundred TV panels, the plunger was examined and it was found that the plunger had score marks most of the way around the periphery, however, the outboard side appeared to be slightly worse.

This was the adjacent sidewall which was intentionally not peppered with molyed-di-sulfide to test the lubricity of the coating. In addition, corners "A and D" which had been given thicker coating deposits, looked significantly better than the opposite corners. A pattern on the coating surface resembling flow lines which radiated outward from the gob impact location in a roughly linear manner were apparent. Due to the thinness and nonleveling nature of the aluminum oxide coating, the stipple surface on the plunger appeared to be virtually unchanged.

The coating thickness on the plunger was fairly uniform except for the added thickness intentionally applied to corners "A and D". It was felt that the results of example 1 were more positive than the results obtained with example 2. The most significant change in the process of example 2 was the use of a high energy ion beam source. The higher arrival energy of the atoms affected the morphology of the coating surface and increased the residual stress in the coating. Also, the sidewall scoring could be caused by increase shear stress on the coating due to a change in the morphology, coupled with high residual stress from deposition conditions.

#### Example 3

A plurality of 3 inch diameter test plungers forming a substrate of 420 stainless steel were stippled in a manner similar to that applied to plungers for forming TV panels. After being coating in a manner hereinafter set forth, the plungers were evaluated in a test furnace.

Typical parameters for the experiments were 850 C glass temperature, 600 C plunger temperature, low humidity, 22 hours testing time, and using television panel glass composition.

Samples were rinsed with isopropyl alcohol (IPA) prior to ultrasonic (US) cycles. Each sample was placed in an evaporating dish, covered with IPA and US cleaned for 15 minutes. Samples were rinsed under running deionized (DI) water and placed in an evaporating dish covered with DI water for another 15 minutes of US cycle.

The samples were then rinsed under running DI water followed by acetone rinse, and dried in a clean drying oven at about 100 C for 15-20 minutes.

The cleaned samples were mounted on a substrate holder, the holder was mounted inside a vacuum chamber.

The vacuum bell was lowered and initial operation was started to pump the chamber down to 50E-3 Torr, and a substrate heater was started at this point. The initial pumping operation was stopped and a high vacuum pump was used to finish the pump down to 5E-6 Torr inside the chamber. Argon was pumped into the chamber and the pressure, DC bias-set and RF were introduced to generate an Ar plasma. The following table sets forth various conditions of Ni/V (92% Ni, 8% V) deposition on 420 SS substrates:

Sample Purpose Pressure Target # Millitorr Volts

71206 Low Pressure 0.8 624

71207 Lowest stable pressure 0.6 647

71208 Hi Pressure & tensile strength 5.0 491

71209 Heat Level 1 0.8 622

71210 Heat Level 2 0.8 619

71211 Cr underlay 750A 0.8 615

71212 DC Bias Level 1 0.8 615

71213 Cr underlay 1000A 0.8 604

71214 DC Bias Level 2 0.8 609



71215 Cr underlay 1000A 0.8 598  
 Sample Current Dep. Temp DC Coating # Amps Time C Bias pm  
 71206 0.49 15 4.5  
 71207 0.46 15 4.5  
 71208 0.62 15 4.5  
 71209 0.49 15 2560 4.5  
 71210 0.49 15 350 4.5  
 71211 0.49 15 4.5  
 71212 0.49 15-100 4.5  
 71213 0.5 15 4.5  
 71214 0.5 15-150 4.5  
 71215 0.51 15 4.5

As noted from the above table, sample #71208 was sputtered under higher pressure (5 millitorr versus an average 0.78 millitorr), and with lower target voltage (491 volts versus the average of 617 volts) than the other samples in the above table. Sample #71208 was the only sample that exhibited delamination problems. Samples #71209 and 71210 were heated to 250 and 300 C, respectively and samples #71212 and 71214 were sputtered under different DC bias levels. Scanning electron microscope analysis indicated that the coatings for all other samples were well adhered and uniform at approximately 4.5 um thickness. All samples, excepting 71208 performed well in nano indentation testing as well.

#### Example 4

Substrates, consisting of stippled 420 stainless steel plunger blanks were prepared, cleaned and tested as set forth in example 3. However, instead of being sputter coated as in example 3, the substrates of this example were coated by electron beam physical vapor deposition (EB-PVD). That is, the stainless steel plunger blanks were mounted on a holder and placed in a vacuum chamber on a rotating fixture. The coating material was placed in a carbon crucible and temporarily covered by a shutter to prevent splattering during the heating process. The initial and differential pumps were started to pump the vacuum chamber down to about 3-4E-6 Torr. At this point cooling water was started, along with the power for the electron beam. The high voltage power control for the electron beam was adjusted to 0.011-0.012 amps according to the level required to cause evaporation without splattering. As the coating material was bombarded by the electron beam it evaporated or sublimed. The shutter was moved aside and the coating material was deposited on the substrate. A sweep of the electron beam was adjusted to maximize available sample.

The above description of parameters for electron beam physical vapor deposition coating were valid for both this example 4 and example 5, however specifically for this example 4 an aluminum oxide target source was placed in the carbon crucible, and a substrate heater was used to achieve a measured temperature of 105 C. The power and sweep were adjusted to allow a coating at an average of 5 angstrom per second. Pressure inside the chamber reached approximate 1E-4 Torr with Oz introduced to the system to assist the formation of the oxide layer. Total deposition time was 35 minutes, with the total deposition according to the crystal readout was 1.04 un. However, according to Dektak measurements total deposition was 1.5 um. The scanning electron microscope results indicated that the Al2O3 coating adhered well to the metal surface of the samples.

#### Example 5

Metal substrates were mounted inside a vacuum chamber as in example 4 above, however magnesium oxide was placed in the carbon crucible as a target source in place of aluminum oxide. A heater was used to bring the vacuum chamber temperature to 75 C. Deposition rate was adjusted to approximate 10 angstroms per second, with beam current set at 0.005 amps. No O2 was introduced into the chamber and pressure inside the chamber averaged 1E-4 Torr. The total deposition time was 67 minutes, with a total deposition of 3 um per the crystal readout. However, the

Dektak measurements showed that a coating thickness of 3.4 um was applied. Glass testing of the plunger blanks was satisfactory with no dulling of the test glass, which is a known indicator of contamination. Analysis of the test glass showed only components of the glass and no residual material from the MgO. Scanning electron microscope results indicated that the coating adhered well to the metal surface of the samples.

Examination of the molten glass corrosion test results from examples 3,4 and 5, indicates that Al<sub>2</sub>O<sub>3</sub>, MgO, Ni/V are all viable candidates as an alternative plunger coating for chrome plating. However, indentation test results showed that Ni/V coating was less brittle.

However, in our overall analysis, it appears that aluminum oxide is our now preferred coating material. The aluminum oxide may be used as a stand alone coating or as the top layer of a duplex coating. A stand alone coating could be used with a deposition process that prevents the microcracking of the alumina on the substrate, however, a bonding coat between the plunger and the Al<sub>2</sub>O<sub>3</sub> functions to provide long life to the plunger by preventing microcracking in the alumina, which would result in oxygen reaching the iron substrate and oxidizing the iron. A bond coat material of commercially pure nickel is preferred between the plunger surface and the Al<sub>2</sub>O<sub>3</sub> coating, although a nickel alloy such as CoNiCrAlY (23% Co, 46.2% Ni, 18% Cr, 12.5% Al, 3% Y by weight), could be used. The bonding coat compensates for the expansion mismatch between the alumina and the iron plunger, which mismatch can result in cracking in the alumina which is brittle.

The bonding or undercoat of nickel or CoNiCrAlY alloy may be applied during the same electron beam physical vapor deposition (EB-PVD) process that applies the Al<sub>2</sub>O<sub>3</sub>.

Both a crucible with the Al<sub>2</sub>O<sub>3</sub> and a crucible with the nickel or the alloy are provided within the vacuum chamber as target materials, and the nickel or alloy containing crucible is initially indexed into position of the electron beam, and after deposition of 1-2 microns of the undercoat, then the Al<sub>2</sub>O<sub>3</sub> crucible is moved into such position so that there is a bond coat between plunger and the alumina protective coating. Finally the alumina oxide layer will be in a 7-15 micron thickness range, whether it is a stand alone coating or in combination with a bond coating. When a bond coating is used, its thickness should be about 1-2 microns. The essentials of the process are an EB-PVD with IBAD, initially applying 1-2 um under/bond coat of nickel, a top coat of 10-15 microns

Al<sub>2</sub>O<sub>3</sub> with a production deposition rate of approximately 50-70 angstroms/sec at a pressure in the range of 10-5 Torr and a tilt angle of about 30-35 degrees from the target source.

Although we have disclosed the now preferred embodiments of the invention, it will be apparent to those skilled in the art that various changes and modifications may be made thereto without departing from the spirit or scope of the invention as set forth in the appending claims.

## **Glass-ceramic coatings for titanium-based metal surfaces**

## **Glass-ceramic coatings for titanium-based metal surfaces**

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Inventor(s):  
ANDRUS RONALD L (US); MACDOWELL JOHN F (US)

Applicant(s):  
CORNING INC (US)

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#### Abstract

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An article of manufacture comprising protectively coated titanium, titanium alloy or titanium aluminide, and a method for making it, wherein the protective coating is an adherent crystalline alkaline earth silicate glass-ceramic coating having a composition consisting essentially, in weight percent on the oxide basis, of about 20-75% total of oxides selected in amounts not exceeding the indicated proportions from the group consisting of up to about 50% BaO, 55% SrO, and 35% CaO, 25-60% of SiO<sub>2</sub> and, as optional constituents, 0-25% MnO, 0-20% MgO, and 0-30% total of other compatible bivalent and trivalent metal oxides. The coating is applied as a continuous glassy coating and is converted to a crystalline glass-ceramic coating by heat treatment.

This invention relates to glass compositions for providing protective coatings on titanium-based metal substrates and more particularly to coated articles composed of or comprising a substrate portion formed of titanium, titanium aluminide or titanium alloy and a coating on the substrate which is a barium silicate or strontium silicate glass-ceramic coating. The coating serves as a chemical barrier against oxidation or other deterioration of the substrate by corrosive agents in the environment, as well as a thermal barrier to prevent rapid heatup of the substrate.

A recently developed series of titanium aluminide intermetallic compounds offers a unique combination of low density, high strength, and sustained resistance to temperatures up to 1000 DEG C. These compounds are being considered for use in airframes, engines, and other components for advanced ultrasonic aircraft such as the national aerospace plane (NASP), where multiple exits from and entries into the earth's atmosphere will be required. This application will

require very high resistance to oxidation and, in at least some cases, high resistance to hydrogen attack over a broad temperature regime.

However, two aluminide candidate materials presently being evaluated, i.e., titanium aluminide in the gamma form (TiAl) and in the super .alpha.-2 form (Ti<sub>3</sub>Al) are both susceptible to oxidation attack, as well as to hydrogen embrittlement at elevated temperatures. Therefore, protective coatings will be required before these lightweight intermetallic compounds can be broadly utilized for space-age aircraft.

A common method of protecting materials from oxidation at elevated temperatures is to apply a continuous monolithic glass coating. This completely encapsulates and isolates the material from the surrounding atmosphere; however, viscous flow of the glass coating may occur when large surface stresses develop during high temperature use. In that case, a glass barrier coating tends to develop thin spots and fails catastrophically.

The high temperature viscosity of the glass coatings may be increased by mixing crystalline materials with the glass frits before application of the coating. However, these glass-crystalline mixtures sinter rather non-uniformly, the crystal size and homogeneity being very difficult to control. Certain portions of the substrate, therefore, tend to be entirely free from crystals, whereas other portions have too many (or too large) crystals to sinter well. A void-free coating with this heterogeneous glass-crystal mixture is thus difficult to obtain.

Polycrystalline ceramic coatings have been proposed as a way to protect superalloy materials from oxidative deterioration. Thus U.S. Pat. Nos. 4,485,151 and 4,535,033 (Stecura) describe the application of insulating layers of stabilized ZrO<sub>2</sub> to such materials via a plasma-spraying technique.

Such procedures involve several steps that are tedious and difficult to control in commercial production. Further, thermal gradients tend to develop during plasma-spraying and introduce defects in the finished coating. Also, the coatings tend to be porous. This permits access of gases, in particular O<sub>2</sub>, H<sub>2</sub>, SO<sub>2</sub>, and water vapor, all of which can contribute to coating failure.

Glass-ceramics per se are of course well known and a wide variety of glass-ceramic compositions for various uses has been developed. U.S. Pat. No. 3,397,076 (Little et al.), for example, describes fused crystallizable ground and cover coats for high temperature alloys in which the major elements are cobalt, nickel, chromium, iron or mixtures. The ground coat is lithium-free and contains 35-65% SiO<sub>2</sub> and 12-45% BaO. Examples also contain substantial amounts of R<sub>2</sub>O, B<sub>2</sub>O<sub>3</sub> and/or TiO<sub>2</sub>.

U.S. Pat. No. 3,467,534 (MacDowell) discloses glass-ceramic articles consisting essentially of 20-70% BaO and 30-80% SiO<sub>2</sub> and having a barium silicate principal crystal phase. A preferred example is described as considered for coating metals. U.S. Pat. No. 3,531,303 (Bahat) discloses glass-ceramic articles in the alkaline earth aluminosilicate field wherein a hexagonal alkaline earth feldspar or a triclinic form is the principal crystal phase. The materials are highly refractory with service temperatures up to 1700 DEG C. and consist essentially of 12-53% SiO<sub>2</sub>, 17-55% RO where RO is 17-50% SrO and 20-50% BaO, 10-58% Al<sub>2</sub>O<sub>3</sub> and a nucleating agent.

U.S. Pat. No. 3,578,470 (Bahat) discloses glass-ceramic materials in the BaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> composition field nucleated with Ta<sub>2</sub>O<sub>5</sub> and/or Nb<sub>2</sub>O<sub>5</sub> that are especially suited to sealing with tungsten or molybdenum and their alloys, while U.S. Pat. No. 3,837,978 (Busdiecker) discloses barium aluminosilicate glass-ceramics nucleated by tin oxide, having a hexacelsian primary crystal phase, and having a coefficient of thermal expansion in the range of 50-170x10<sup>-7</sup> / DEG C.

Notwithstanding the fact that both glass-ceramic and coating technologies are highly developed, there remains a need for new protective coating formulations which could protect titanium,

titanium alloys and titanium aluminide compounds from oxidation and other deterioration at high temperatures. It is accordingly a principal object of the present invention to provide a reliable and reproducible oxygen barrier coating for titanium, titanium alloy and titanium aluminide bodies or components that are required to operate at elevated temperatures.

Another object is to provide such a coating that is more effective, and easier to apply, than previously known coatings.

A further object is to provide a protective coating for titanium alloys and titanium aluminides that is non-porous, continuous and free from defects such as pinholes and cracks, and thus a barrier to the diffusion of oxygen as well as hydrogen and other corrosive gases.

A still further object is to provide a barrier coating that adheres tightly and resists spalling during thermal cycling.

Another object is to provide an oxygen barrier coating material that exhibits the excellent flow characteristics of a glass coating as it is fired in one temperature range, and becomes resistant to flow (due to crystallization) as it is heated in a higher temperature range.

A further object is to provide a titanium alloy or aluminide substrate or article supporting a glass-ceramic barrier coating that adapts the substrate to very high operating temperatures.

A still further object is to provide a useful degree of thermal insulation to titanium, titanium alloy, or titanium aluminide surfaces.

#### SUMMARY OF THE INVENTION

One difficulty associated with the application of protective coatings to titanium aluminide substrates relates to the fact that surface oxidation of these substrates prior to or during coating application must be taken into account. The resulting  $\text{TiO}_2$ - $\text{Al}_2\text{O}_3$  surface oxidation products provide a surface having a lower thermal expansion coefficient than that of superalloy surfaces comprising one or more of the oxides of nickel, cobalt, or iron.

The present invention provides a method for protecting titanium aluminide surfaces from oxidation or other attack by the application of one of a family of alkaline earth silicate glass-ceramic coating compositions thereto. These compositions provide excellent flow, crystallization and compatible bonding characteristics as applied to titanium aluminide substrates. Similar characteristics are imparted through application of the glass-ceramic coating compositions to titanium and titanium alloy substrates. The coating compositions are characterized alkaline earth silicates wherein barium, strontium and/or calcium constitute the alkaline earth oxides.

More particularly, the coatings have compositions consisting essentially, in weight percent on the oxide basis, of about 20-75% total of oxides selected in amounts not exceeding the indicated proportions from the group consisting of up to about 50%  $\text{BaO}$ , 55%  $\text{SrO}$ , and 35%  $\text{CaO}$ , 25-60% of  $\text{SiO}_2$  and, as optional constituents, 0-25%  $\text{MnO}$ , 0-20%  $\text{MgO}$ , and 0-30% total of other compatible bivalent and trivalent metal oxides. To apply the coatings, glasses of the specified composition are applied to a titanium aluminide or titanium alloy surface to provide a continuous glassy coating thereon, and the coating is then crystallized by heat treatment to provide an adherent, densely crystalline glass-ceramic protective coating.

The invention further resides in a coated article or substrate formed of a metal selected from the group consisting of titanium, titanium alloys and titanium aluminides, wherein the metal is protected from oxidation and other types of corrosion by an adherent crystalline alkaline earth silicate glass-ceramic coating having a composition as above described. Through the use of these protective glass-ceramic coatings the article may be adapted to operate safely at

temperatures up to 1000 DEG C. in an oxygen-containing environments. Recent data suggest good resistance to hydrogen diffusion as well.

#### DETAILED DESCRIPTION

The coating compositions of the invention exhibit excellent flow and adherence to titanium aluminide surfaces during firing in air or other suitable atmospheres at temperatures above the softening point of the glass. Typical firing temperatures are in the range of 800-1100 DEG C. No spalling due to thermal expansion mismatch or other incompatibility with the titanium aluminide substrate is observed upon cooling the fired coating.

A key feature provided by the coatings of the invention is that of achieving an appropriate balance between adequate viscous flow of the glass during the early firing stages and dense crystallization of the coating prior to completion of the firing cycle. Premature crystallization results in insufficient flow and a rough, porous coating.

Surprisingly, the achievement of adequate flow and adherence characteristics in these coatings does not require the use of crystallization retardants such as  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$ . Such additives may be present if desired, but coatings of equivalent or superior quality may be achieved, particularly on Ti3 Al substrates, in compositions free of these additives.

As is known, ceramics having a high expansion coefficient commonly contain rather large quantities of alkali oxides ( $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ , or  $\text{K}_2\text{O}$ ). However, these alkali ions are extremely mobile in most ceramic structures at high temperatures, and readily exchange for other ions. Therefore, they must be eliminated as major constituents in coatings that must continually operate at high temperatures.

Small additions, generally less than 5 mole percent, of other glass-modifying oxides, such as  $\text{CeO}_2$ ,  $\text{TiO}_2$ ,  $\text{Nb}_2\text{O}_5$  and  $\text{B}_2\text{O}_3$ , can in some cases improve the flow and appearance of the coatings. Mixed barium magnesium and calcium magnesium silicate coatings comprising  $\text{B}_2\text{O}_3$  are known, for example from U.S. Pat. Nos. 4,256,796, 4,358,541 and 4,385,127. However, the presence of a residual glassy or crystalline phase comprising this oxide tends to allow the crystals in the microstructure to move and flow at temperatures much below the solidus of the primary refractory silicate phases. Accordingly, the present coatings are most preferably formulated with little or no boric oxide.

The transition metal oxides  $\text{FeO}$  (or  $\text{Fe}_2\text{O}_3$ ) and  $\text{MnO}$ , as well as the alkaline earth oxide  $\text{MgO}$ , appear to be effective in some of these composition systems in promoting a continuous, well-flowed glass coating prior to crystallization without unduly reducing the refractoriness of the coatings. These therefore constitute the preferred optional oxide additives for the protective coating of titanium aluminide substrates.

Based on the foregoing considerations, a preferred family of alkaline earth silicate glass-ceramic coating formulations has been identified. In these compositions, the optional additives to the ( $\text{BaO}$ ,  $\text{SrO}$ ,  $\text{CaO}$ )- $\text{SiO}_2$  base compositions are selected in the indicated proportions from the group consisting of 0-25%  $\text{MnO}$ , 0-25%  $\text{FeO}$ , 0-20%  $\text{MgO}$ , 0-10%  $\text{ZrO}_2$ , 0-10  $\text{Al}_2\text{O}_3$  and up to 35% total of  $\text{MnO}+\text{FeO}+\text{MgO}+\text{ZrO}_2 +\text{Al}_2\text{O}_3$ .

The glass-ceramic compositions of the invention are most conveniently applied to titanium aluminide surfaces in the form of fine glass powders. Typically, the glasses are melted and converted from the melt into granular glass by drigaging or the like, and are then milled to provide fine glass powder. The particle sizes of the milled glass are typically in the 5-20 micron range, although smaller particle sizes may be preferred where very thin coatings are required.

The surface of a selected titanium aluminide body or body comprising a titanium aluminide surface may be coated with the powdered glass in any conventional manner. The method we

prefer is electrostatic spraying, wherein electrostatically-charged, dry glass powder is very uniformly sprayed onto the aluminide body, which is supported on an oppositely charged wire mesh screen. Alternatively, the powdered glass may be mixed with a suitable medium, e.g., water or an organic vehicle, applied uniformly over the glass surface and dried.

The glass powder-coated aluminide body is then heated to a temperature of 800-1100 DEG C. This softens the glass particles and produces a dense, smooth, well-formed continuous glass coating that is essentially free from crystallization. The glass-coated body is then heated for a longer time or to a somewhat higher temperature. This completes the development of crystal phases to form a dense, strong, refractory, crystalline coating.

The invention is further illustrated in Table I below by specific examples of glass-ceramic compositions that may be applied as coatings to titanium aluminide bodies in accordance with the invention. Properly applied, these materials yield smooth, adherent, non-porous coatings that have little or no tendency to spall during temperature cycling.

To prepare coating material from these compositions, glass batches of corresponding composition are mixed and melted in platinum crucibles at 1600-1650 DEG C. for two hours. The glass melts thus obtained are then poured into water to quench and granulate the glass. The granular glass (drillage) is thereafter ball milled with alumina cylinders for 4 to 8 hours to provide powdered glass with an average particle size of about 10 micrometers.

TABLE I

---

Coating Compositions

---

1 2 3 4 5 6 7 8 9

---

SiO<sub>2</sub>

36.4 34.9 32.5 31.9 32.0 34.8 33.3 29.8 29.4

BaO 46.5 44.5 41.5 40.8 40.9 44.5 42.6 38.1 37.6

SrO ----- 25.7 25.4

CaO 17.0 ----- 15.6 ---

MnO -- 20.6 19.2 -- 18.9 -----

FeO ----- 19.1 -----

MgO ----- 11.7 -----

Al<sub>2</sub>O<sub>3</sub>

--- 6.9 ----- 6.3 --

ZrO<sub>2</sub>

----- 8.2 8.2 8.9 8.6 -- 7.6

---

10 11 12 13 14 15 16 17

---

SiO<sub>2</sub>

36.9 33.9 41.7 38.6 54.2 46.2 40.4 45.5

BaO 31.8 43.3 42.7 --- 39.4 34.4 --

SrO ----- 50.0 ----- 26.2

CaO --- 15.6 -- 22.5 14.4 25.2 28.3

MnO 21.7 20.0 -- 11.4 7.1 -----

MgO ----- 16.2 -----

Al<sub>2</sub>O<sub>3</sub>

-- 2.9 -----

ZrO<sub>2</sub>

9.5 -----

---

To characterize the crystallization behavior of the above compositions, powdered glasses

produced as described are dry-pressed into cylinders 1/2" in diameter. These are then heat treated at temperatures of 800-1200 DEG C. for 1/2-1 hour to determine the sintering characteristics and density (porosity) of the compositions. Additionally, 4".times.1/4".times.1/4"bars are pressed and fired to determine the thermal expansion coefficients of the crystalline materials.

In some cases X-ray diffraction analyses are conducted on fired samples to determine crystal phases developed during firing. In general these analyses reveal complex patterns of calcium, strontium, and barium silicates, substantially modified in some cases by the addition of other oxides. Specific examples of major crystal phases which have been identified include Ba<sub>1.55</sub>Ca<sub>.45</sub>SiO<sub>4</sub>, BaSrSi<sub>3</sub>O<sub>8</sub>, BaMg<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> and Ca<sub>2</sub>BaSi<sub>3</sub>O<sub>9</sub> (Walstromite).

Coatings of the compositions thus evaluated are next applied to titanium aluminide substrates to confirm the compatibility of the glass and glass-ceramic materials therewith. The coatings are applied in thicknesses between 20 and 100 micrometers to Ti<sub>3</sub>Al coupons of 2 mm thickness using electrostatic spraying. The surfaces of the coupons are cleaned and grit-blasted prior to coating. Each glass-coated coupon is then fired to a temperature of 1000 DEG C. for one hour, using a furnace heating rate of approximately 75 DEG C. per minute. Although both air and helium atmospheres are used during firing and appear to yield excellent coatings, air is preferred because of its appreciably lower cost.

Illustrative results from evaluations such as described above are reported in Table II below. The example numbers of Tables I and II correspond for cross reference. Included in Table II for each of the Table I compositions are density and thermal coefficient of expansion (TCE) data as determined on pressed crystallized samples, as well as a description of the appearance of coatings of the crystallized glass-ceramics as applied to Ti<sub>3</sub>Al substrates.

As the coating descriptions indicate, small seed and pinhole defects are observed in some of the coatings, particularly if very thin, and minor edge spalling is observed in one case. However, it is anticipated that fine tuning of the processing will readily avoid these minor conditions.

TABLE II

Coating Properties		
Density	TCE	Coating Description
Example		
(g/cc) (.times.10@7 DEGC.)		
(Ti <sub>3</sub> Al Substrate)		
1 3.234	129.3	grey translucent
2 3.243	141.1	finely textured grey
3 3.257	65.4	opaque brown/silver grey surface
4 3.313	97.7	smooth glossy brown/few pinholes
5 3.345	115.2	wrinkled "metallic" vio.-grey
6 3.744	96.0	slt. rippled transparent
7 3.158	49.8	transparent smooth, seeds and pinholes
8 3.472	94.1	grey translucent, pinholes
9 3.535	97.9	clear transparent, v. fine seed
10 3.081	117.7	textured black
11 3.218	80.6	grey surface crystals on dk. brown coating
12 3.562	111.9	pinholes, blistered translucent grey-brown
13 2.963	103.9	textured glossy red-brown



14 2.971 89.0 translucent grey/some seed,  
pinholes  
15 3.277 84.0 smooth translucent, some seed  
and edge spalling  
16 3.496 99.7 lt. grey brown, some pinholes,  
v.f. surface cracks  
17 3.071 111.6 translucent grey; pinholes, fine  
surface cracks

---

Unexpectedly, scanning electron micrographs of selected coatings from Table II indicate that, in most cases, no oxide interface is present between the Ti3 Al substrate and the glass-ceramic coating. This is in contrast with the appearance of uncoated air-fired Ti3 Al which, under the firing conditions used to apply these protective coatings, develops a loose oxide layer of 5 to 10 .mu.m thickness.

The absence of an oxidation layer is presently attributed to the dissolution of surface TiO2 and Al2 O3 byproducts of titanium aluminide oxidation by the glass during firing. Thus in addition to providing excellent oxidation protection, anticipated to be equivalent to that afforded to superalloy substrates by certain of these coatings, the use of a helium atmosphere during coating application is not required. Good coating adherence even to partially oxidized surfaces can apparently be achieved. Of course, the final coating would be expected to show significant increases in TiO2 and Al2 O3 content in the interfacial region as dissolution of surface oxides occurs, but there is no evidence that this effect is harmful to the adherence and other properties of the coating.

As expected, equivalent coating properties for these compositions are observed when a gamma-titanium aluminide (TiAl) rather than a Ti3 Al substrate is treated. Table III below reports coating results for selected compositions from Table I as applied to TiAl coupons following the coating procedure described above.

TABLE III

---

Coating Properties  
TCE Coating Description  
Example  
(.times.10@7 DEGC.)  
(TiAl Substrate)

---

1 129.3 translucent, hazy, porous, adherent, no  
spalling, but too thin  
3 65.4 smooth, dark, transparent, adherent, no  
spalling; seeds, pinholes where too thin  
8 94.1 dark, transparent, smooth, adherent, no  
spalling  
10 117.7 dark, translucent, smooth, adherent, no  
spalling, pinholes from seed blisters  
14 89.0 porous, translucent, grey, adherent, no  
spalling, discontinuous  
15 84.0 porous, dark, translucent grey, adherent,  
no spalling, discontinuous

---

These results, in combination with similar results for other coating compositions applied to TiAl within the scope of the invention, have demonstrated complete freedom from spalling and therefore good physical and chemical compatibility with these substrates. Again, minor coating continuity difficulties including pinholes may be corrected with thicker coatings and/or routine

process modifications.

The use of the glass-ceramic coating compositions of the invention to provide protective coatings of high quality on titanium and titanium alloy substrates provides similar levels of substrate protection. Of course, in contrast to the titanium aluminides, which are based largely on the titanium intermetallic compounds Ti<sub>3</sub>Al and/or TiAl and consist predominantly of titanium and aluminum, the commercial titanium alloys contain mostly titanium metal with only minor additions of other elements. Nevertheless, good adherence and coating quality are obtained with these substrates as well.

Representative commercial titanium alloy compositions which may be provided with glass-ceramic coatings in accordance with the invention are set out in Table IV below. The proportions of titanium and alloying elements making up each of the alloys shown are reported in parts by weight.

TABLE IV

---

Titanium Alloys  
Alloy Ti Al Nb V Mo Sn Zr Cr

---

Ti-6-4 90 6 -- 4 -- -- -- --

Ti-6-2-4-2

86 6 -- -- 2 2 4 --

Ti-8-1-1

90 8 -- 1 1 -- -- --

Ti-5-2.5

92.5 5 -- -- -- 2.5

-- --

Ti-6-6-2

86 6 -- 6 -- 2 -- --

Ti-6-2-4-6

82 6 -- -- 6 2 4 --

Ti-15-3-3-3

76 3 -- 15 -- 3 -- 3

Ti-13-11-3

73 3 -- 13 -- -- -- 11

Ti-3-8-6-4-4

75 3 -- 8 4 -- 4 6

Ti-10-2-3

85 3 -- 10 -- -- -- (2Fe)

---

An illustrative procedure for applying a protective glass-ceramic coating to a typical titanium alloy substrate is as follows. A sample of the alloy designated as Ti-6-4 alloy in Table IV above, consisting of about 6 weight percent Al, 4 weight percent V, and the balance Ti, is selected for coating. A powdered glass for a glass-ceramic coating is then selected, the glass selected having a composition, in weight percent, of about 38.3% SiO<sub>2</sub>, 33.1% SrO, 5.9% ZrO<sub>2</sub>, and 22.7% MnO. A powder of this glass is prepared by crushing glass ribbon of the selected composition and then grinding the crushed glass to reduce the average particle size to about 8 .mu.m.

A sample of the titanium Ti-6-4 alloy is next prepared for coating by grit-blasting with 220 grit alumina. Thereafter the sample is washed in soapy water, rinsed in distilled water, air-dried at 110 DEG C., and cooled to room temperature. The sample is next coated with the powdered glass, using a two-step coating procedure to insure good substrate coverage. A slurry of the glass powder is first prepared and applied to the sample by dipping. The slurry consists of about 40 grams of glass powder and 60 ml of ethyl acetate. After air-drying, the dried slurry coating is then overcoated with an additional coating of the same slurry, this overcoating being applied by

electrostatic spraying in accordance with known practice.

The coated sample thus provided is next heat-treated to sinter and crystallize the powdered glass coating. Heat treatment comprises firing the sample in a helium-rich atmosphere at 850 DEG C. for one hour. Post-heat-treatment examination of the sample shows good coating flow and full crystallization of the glass, with excellent adherence of the coating to the alloy substrate.

The coated titanium alloy sample thus provided is tested for oxidation resistance, along with an uncoated alloy sample, using a cyclic thermal oxidation test. Multiple thermal cycles are used, each cycle comprising plunging the sample into a 650 DEG C. furnace (air atmosphere) for 65 minutes, following by sample removal and a 45 minute interval in air at room temperature.

The results of this test demonstrate excellent oxidation resistance in the coated sample. While the uncoated titanium alloy sample showed a weight gain of over 0.9 mg/cm<sup>2</sup> due to oxygen pick-up through only 48 thermal oxidation cycles, the sample provided with the glass-ceramic coating gained less than 0.08 mg/cm<sup>2</sup> through 821 such cycles. Most importantly, the glass-ceramic coating on the thermally cycled sample exhibited no change in appearance, and remained well-adhered to the titanium alloy substrate.

While the invention has been particularly described above with respect to specific materials and specific procedures, it will be recognized that those materials and procedures are presented for purposes of illustration only and are not intended to be limiting. Thus numerous modifications and variations upon the compositions and processes specifically described herein may be resorted to by those skilled in the art within the scope of the appended claims.

We claim:

1. A method for protecting a substrate formed of a metal selected from the group consisting of titanium, titanium aluminides and titanium alloys from oxidation and chemical attack which comprises the steps of: applying to a surface of the substrate a continuous glassy coating of an alkaline earth silicate glass having a composition consisting essentially, in weight percent on the oxide basis, of about 20-75% total of oxides selected in amounts not exceeding the indicated proportions from the group consisting of up to about 50% BaO, 55% SrO, and 35% CaO, 25-60% of SiO<sub>2</sub> and, as optional constituents, 0-25% MnO, 0-20% MgO, and 0-30% total of other compatible bivalent and trivalent metal oxides; and crystallizing the continuous glassy coating by heat treatment to provide an adherent, densely crystalline glass-ceramic coating on the substrate surface.
2. A method in accordance with claim 1 wherein the substrate is a titanium aluminide and wherein the optional constituents in the alkaline earth silicate glass are selected in the indicated proportions from the group consisting of 0-25% MnO, 0-25% FeO, 0-20% MgO, 0-10% ZrO<sub>2</sub>, 0-10 Al<sub>2</sub> O<sub>3</sub> and up to 35% total of MnO+FeO+MgO+ZrO<sub>2</sub> +Al<sub>2</sub> O<sub>3</sub>.
3. A coated article composed of a metal selected from the group consisting of titanium, titanium aluminides and titanium alloys wherein the metal is protected from oxidation by an adherent crystalline alkaline earth silicate glass-ceramic coating having a composition consisting essentially, in weight percent on the oxide basis, of about 20-75% total of oxides selected in amounts not exceeding the indicated proportions from the group consisting of up to about 50% BaO, 55% SrO, and 35% CaO, 25-60% of SiO<sub>2</sub> and, as optional constituents, 0-25% MnO, 0-20% MgO, and 0-30% total of other compatible bivalent and trivalent metal oxides.
4. A coated article in accordance with claim 3 which is composed of titanium aluminide and wherein the optional constituents present in the crystalline alkaline earth aluminosilicate glass-ceramic coating are selected in the indicated proportions from the group consisting of 0-25% MnO, 0-25% FeO, 0-20% MgO, 0-10% ZrO<sub>2</sub>, 0-10 Al<sub>2</sub> O<sub>3</sub> and up to 35% total of

MnO+FeO+MgO+ZrO<sub>2</sub> +Al<sub>2</sub> O<sub>3</sub>.

5. A coated article in accordance with claim 4 which is resistant to oxidation at temperatures up to 1000 DEG C. in an oxygen-containing environment.

## Hermetic substrate coatings in an inert gas atmosphere

## Hermetic substrate coatings in an inert gas atmosphere

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Inventor(s):

HALUSKA LOREN ANDREW (US)

Applicant(s):

DOW CORNING (US)

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Equivalents:

### Abstract

The present invention relates to a method of forming a ceramic or ceramic-like coating on a substrate in the absence of oxygen. The method comprises coating the substrate with a solution comprising a solvent and one or more preceramic materials selected from the group consisting of

hydrogen silsesquioxane and hydrolyzed or partially hydrolyzed  $R_xSi(OR)_{4-x}$  wherein R is independently selected from the group consisting of alkyl, aryl and unsaturated hydrocarbons and x is 0-2. The solvent is evaporated and a preceramic coating thereby deposited on the substrate. The preceramic coating is then ceramified by heating the coated substrate to a temperature of between about 500 up to about 1000 C. under an inert gas atmosphere to thereby produce a ceramic or ceramic-like coating on the substrate. The process of the invention is useful for forming protective coatings on any substrate prone to oxidation at the temperature necessary for ceramification. The present invention also relates to the formation of additional ceramic coatings on the ceramic or ceramic-like coating formed above

## FIELD OF INVENTION

This invention relates to the protection of substrates such as electronic devices with surface-applied ceramic coatings of materials such as amorphous silica, silicon, silicon carbide, silicon nitride and silicon carbonitride.

## BACKGROUND OF THE INVENTION

Electronic devices, to be serviceable under a wide variety of environmental conditions, must be able to withstand moisture, heat and abrasion, among other stresses. A significant amount of work has been reported directed toward various protective measures to minimize the exposure of these devices to the above conditions and thereby increase their reliability and life. Most of these measures, however, suffer from various drawbacks.

For instance, early measures involved potting electronics within a polymeric resin and, thereby, reducing environmental exposure. These methods proved to be of limited value, however, since most resins are not impermeable to environmental moisture and they generally add extra size and weight.

A second method of protection involves sealing the device within a ceramic package. This process has proven to be relatively effective in increasing device reliability and is currently used in select applications. The added size, weight and cost involved in this method, however, inhibits widespread application in the electronic industry.

Recently, the use of lightweight ceramic coatings has been suggested. For instance, Haluska et al. in U.S. Pat. Nos. 4,749,631 and 4,753,856, which are incorporated herein in their entirety by reference, disclose silicon containing coatings produced by applying solutions of silicon alkoxides or silicon alkoxides and metal oxide precursors, respectively, to an electronic device and then ceramifying in air by heating to temperatures of 200-1000 DEG C. These references also describe the application of other coatings containing silicon carbon, silicon nitrogen or silicon carbon nitrogen onto the initial silica layer for added protection. The ceramic coatings produced thereby have many desirable characteristics such as microhardness, moisture resistance, ion barrier, adhesion, ductility, tensile strength and thermal expansion coefficient matching which provide excellent protection to the underlying substrate.

Haluska et al. in U.S. Pat. Nos. 4,756,977, 4,753,855 and 4,822,697 also disclose light-weight ceramic coatings for electronics obtained from hydrogen silsesquioxane resin (H-resin), H-resin with a metal oxide precursor and H-resin with a platinum catalyst, respectively. The process comprises dissolving the H-resin, H-resin and metal oxide, or H-resin and the catalyst in a solvent, evaporating the solvent, and ceramifying in air at temperatures in the range of 200-1000 DEG C. The silica coating may be further coated with additional layers of silicon carbon, silicon nitrogen or silicon carbon nitrogen.

As noted, the above ceramic coating processes involve heating the electronic devices to temperatures of 200-1000 DEG C. in an atmosphere containing oxygen. When certain metals within the devices are exposed to these conditions, however, they begin to deteriorate through oxidation. For instance, when copper is heated to temperatures above 200-250 DEG C. in the presence of oxygen, it oxidizes to CuO which destroys the integrity of the metal and, thus, the electronic device. Moreover, if one attempts to avoid the above destructive effects by keeping the temperature below the oxidation threshold, ceramification takes so long that the process is not commercially feasible.

Wagner et al. in Industrial and Engineering Chemistry, 44(2), 321-326 (1952) reported heating H-resin (silicon oxyhydride) at temperatures as low as 350 DEG C. in an inert atmosphere and observing hydrogen evolution. This reference, however, does not disclose the utility of applying a coating to a substrate under said conditions.

Glasser et al. in J. Non-crystalline Solids, 63 (1984), 209-221, reported applying a nitrided silica coating on a silicon wafer by heating a hydrolyzed solution of tetraethoxysilane in a flowing nitrogen or ammonia atmosphere. This reference, however, discloses that a significant amount of nitrogen from the atmosphere was incorporated into said coating.

Haluska et al. in U.S. Pat. No. 4,826,733 teach the formation of silicon nitride ceramic coatings on electronic devices in an oxygen free environment. The process disclosed therein is a low temperature method whereby a planarizing or passivating coating is formed by dissolving a silicon nitride compound in a solvent, coating the substrate with said solution, evaporating the solvent and ceramifying by heating to temperatures of 200-400 DEG C. in the absence of air. This reference, however, does not teach the use of silicon compounds other than those containing nitrogen.

The present inventors have now discovered that they can apply a ceramic or ceramic-like coating from materials selected from the group consisting of hydrogen silsesquioxane resin or hydrolyzed or partially hydrolyzed  $R_x Si(OR)_{4-x}$ , wherein R is independently selected from the group consisting of alkyl, aryl and unsaturated hydrocarbons and x is 0-2, in an inert gas atmosphere at temperatures of 500-1000 DEG C.

#### SUMMARY OF THE INVENTION

The present invention relates to a method of forming a ceramic or ceramic-like coating on a substrate in the absence of oxygen. The method comprises coating the substrate with a solution comprising a solvent and one or more preceramic materials selected from the group consisting of hydrogen silsesquioxane resin (H-resin) and hydrolyzed or partially hydrolyzed  $R_x Si(OR)_{4-x}$  wherein R is independently selected from the group consisting of alkyl, aryl and unsaturated hydrocarbons and x is 0-2. The solvent is evaporated and a preceramic coating thereby deposited on the substrate. The preceramic coating is then ceramified by heating the coated substrate to a temperature of between about 500 up to about 1000 DEG C. under an inert gas atmosphere to thereby produce a ceramic or ceramic like coating on the substrate.

The process of the invention is useful for forming protective coatings on any substrate prone to oxidation at the temperature necessary for ceramification. In particular, however, the process is advantageous for sealing electronic devices which contain copper or other metals subject to oxidation.

The present invention also relates to the formation of additional ceramic coatings on the coating formed above. In a dual layer system, the second passivation layer may comprise silicon containing coatings, silicon carbon-containing coatings, silicon nitrogen-containing coatings, silicon carbon nitrogen containing coatings or an additional coating as formed above. In a triple layer system, the second passivation layer may comprise silicon carbon-containing coatings, silicon nitrogen-containing coatings, silicon carbon nitrogen containing coatings or an additional

coating as formed above and the third barrier coating may comprise silicon coatings, silicon carbon-containing coatings, silicon nitrogen-containing coatings, and silicon carbon nitrogen containing coatings.

The additional coating layers described above may be deposited using a number of techniques including, but not limited to, chemical vapor deposition, plasma enhanced chemical vapor deposition, metal assisted chemical vapor deposition and/or ceramification of a preceramic polymer.

#### DETAILED DESCRIPTION OF THE INVENTION

The instant invention is based on the discovery that materials selected from the group consisting of H-resin and hydrolyzed or partially hydrolyzed  $R_x Si(OR)_{4-x}$  can be converted to ceramic or ceramic-like coatings in an inert gas atmosphere at temperatures of about 500-1000 DEG C. Since the ceramification of such preceramic materials had previously been effected by heating in reactive atmospheres such as air or ammonia, the discovery that ceramic or ceramic-like coatings could be formed in an inert atmosphere was unexpected. Similarly it was unexpected that coatings formed in an inert atmosphere would have utility as protective coatings for electronic devices.

The invention also relates to the discovery that the above coatings of this invention can be overcoated with additional silicon, silicon nitrogen, silicon carbon or silicon carbon nitrogen containing passivating and barrier coatings which are deposited in an inert gas or ammonia atmosphere.

The single and multilayer coatings taught herein are particularly useful in providing protective coatings on substrates subject to oxidation when exposed to elevated temperatures in an atmosphere containing oxygen. The choice of substrates and devices to be coated by the instant invention, however, is limited only by the need for thermal and chemical stability of the substrate at the temperature and atmosphere utilized in the present invention. Additionally, the coatings taught herein may serve as dielectric layers, doped dielectric layers to produce transistor like devices, pigment loaded binder systems containing silicon to produce capacitor and capacitor like devices, multilayer devices, 3-D devices, silicon on insulator devices, super lattice devices and the like.

As used in the present invention, the expression "ceramic-like" refers to those pyrolyzed materials which are not fully free of residual carbon and/or hydrogen but which are otherwise ceramic in character; the expression "planarizing coating" refers to a coating which provides a surface barrier layer that is less irregular than the surface prior to application of the coating; the expressions "electronic device" or "electronic circuit" include, but are not limited to silicon based devices, gallium arsenide based devices, focal plane arrays, opto-electronic devices, photovoltaic cells and optical devices; and the expression "hydrolyzed or partially hydrolyzed" is used to designate a silane or mixture of silanes which have been treated with aqueous, basic or acidic conditions so as to hydrolyze either all or a portion of the hydrolyzable substituents on the silane.

In the present invention, the first ceramic or ceramic-like layer may be formed by a process which comprises coating the substrate with a solution comprising a solvent and one or more preceramic materials selected from the group consisting of H-resin and hydrolyzed or partially hydrolyzed  $R_x Si(OR)_{4-x}$  wherein R is independently selected from the group consisting of alkyl, aryl and unsaturated hydrocarbons and x is 0-2. The solvent is evaporated leaving a preceramic coating deposited on the substrate. The coated substrate is then heated to a temperature of between about 500 to about 1000 DEG C. in an inert gas atmosphere to form the coating.

The preceramic materials which are useable in the invention include hydrogen silsesquioxane resin (H-resin),  $R_x Si(OR)_{4-x}$ , or combinations of any of the above materials wherein R is an alkyl of 1-20 carbon atoms such as methyl, ethyl, propyl etc., an aryl such as phenyl, or an unsaturated

hydrocarbon such as vinyl or allyl and x is 0-2. H-resin can be formed by the process of Frye et al. in U.S. Pat. No. 3,615,272, which is incorporated herein by reference. This material has the basic structure  $(\text{HSiO}_3/2)_n$  wherein n is generally 10-1000. The resin has a number average molecular weight of from about 800-2900 and a weight average molecular weight of between about 8000-28,000. When ceramified, this material yields a ceramic or ceramic-like coating essentially free of Si-H bonds.

Compounds of the formula  $\text{R}_x \text{Si}(\text{OR})_{4-x}$  can be divided into 2 distinct types. The first type includes compounds in which the silicon is substituted by groups other than the hydrolyzable substituents, i.e. x is 1-2. These compounds form ceramic or ceramic-like coatings containing residual 'R'. Compounds wherein x=2 are generally not used alone as cyclic structures are generated during pyrolysis, but some of said compounds may be cohydrolyzed with other preceramic compounds. Specific compounds of this first type include monomethyltriethoxysilane, monophenyltriethoxysilane, diethyldiethoxysilane, monomethyltrimethoxysilane, monophenyltrimethoxysilane and monovinyltrimethoxysilane.

The second type of compounds with the formula  $\text{R}_x \text{Si}(\text{OR})_{4-x}$  are those in which the silicon is solely bound to hydrolyzable substituents (i.e. x=0). The coatings produced by these compounds are essentially devoid of any residual organic (R) content. Examples of such compounds include, but are not limited to organic orthosilicates of the formula  $\text{Si}(\text{OR})_4$  wherein R is preferably an alkyl of 1-4 carbon atoms such as methyl, ethyl, propyl etc., an aryl such as phenyl or an unsaturated hydrocarbon radical such as vinyl or allyl. Specific compounds of the above type include tetramethoxysilane, tetraethoxysilane, tetrapropoxysilane, and tetrabutoxysilane.

Additional materials which may function equivalently, but do not fit into the above groups, include condensed esters of the formula  $(\text{RO})_3 \text{SiOSi}(\text{OR})_3$ , disilanes of the formula  $(\text{RO})_x \text{R}_y \text{SiSiR}_y (\text{OR})_x$ , compounds such as  $\text{SiOC}$  wherein the carbon containing group is hydrolyzable under the thermal conditions, or any other source of  $\text{SiOR}$ .

The solvent to be utilized in the instant invention can be any agent or mixture of agents which will dissolve the preceramic material without altering the ceramic coating produced thereby. These solvents can include, for example, alcohols such as ethyl or isopropyl, aromatic hydrocarbons such as benzene or toluene, alkanes such as n-heptane or dodecane, ketones, esters or glycol ethers, in an amount sufficient to dissolve the above materials to low solids. For instance, enough of the above solvent can be included to form a 0.1-35 weight % solution.

If H-resin is utilized, the solution may be catalyzed by the simple addition of a platinum or rhodium catalyst which assists in increasing the rate and extent of ceramification. Any platinum or rhodium compound or complex which can be solubilized in this solution will be operable. For instance, an organoplatinum composition such as platinum acetylacetonate or rhodium catalyst  $\text{RhCl}_3 \cdot (\text{CH}_3\text{CH}_2\text{CH}_2\text{S})_3$ , obtained from Dow Corning Corporation, Midland, Mich. are all within the scope of this invention. The above catalysts are generally added to the solution in an amount of between about 15 to 200 ppm platinum or rhodium based on the weight of resin in solution.

The solution containing the preceramic material and solvent is coated onto the substrate. The method of coating can be, but is not limited to, spin coating, dip coating, spray coating or flow coating. The solvent in the solution is allowed to evaporate by drying and a preceramic coating thereby deposited. It is to be noted that when spin coating is utilized, an additional drying period is generally not necessary as the spinning tends to drive off the solvent.

The preceramic coating is ceramified to a hermetic coating by heating the coated device to 500-1000 DEG C., preferably 600-800 DEG C., under an inert gas atmosphere. Any method of heating such as the use of a convection oven or radiant or microwave energy is generally functional herein. Additionally, the rate of heating is generally not critical, but it is most practical and preferred to heat the substrate as rapidly as possible.



Any inert gas atmosphere such as argon or helium may be utilized in the above ceramification step. It is essential, however, to exclude air since even minor amounts of oxygen may affect the integrity of a metal.

In a typical ceramification procedure, the coated substrate may be placed in a convection oven and a continuous flow of inert gas introduced (with the exclusion of oxygen). The temperature in the oven is then raised to the desired level (such as about 600 DEG C.) and maintained for the desired time (such as about 0.5-3 hours).

By the above method a thin (less than 2 microns) ceramic or ceramic like planarizing coating is produced on the substrate. The coating smooths the irregular surfaces of various substrates and has excellent adhesive properties. In addition, the coating may be covered by other coatings such as additional coatings as formed above, silicon containing coatings, silicon carbon containing coatings, silicon nitrogen containing coatings and/or silicon nitrogen carbon containing coatings which provide additional protection to the substrate.

In a dual layer system, the second passivation layer may comprise silicon containing coatings, silicon carbon-containing coatings, silicon nitrogen-containing coatings, silicon carbon nitrogen containing coatings or an additional coating as formed above. In a triple layer system, the second passivation layer may comprise silicon carbon-containing coatings, silicon nitrogen-containing coatings, silicon carbon nitrogen containing coatings or an additional coating as formed above and the third barrier coating may comprise silicon coatings, silicon carbon-containing coatings, silicon nitrogen-containing coatings, and silicon carbon nitrogen containing coatings.

The passivating coating may be applied by means of (i) coating the first ceramic or ceramic-like layer with a solution comprising a solvent and a preceramic polymer precursor such as polycarbosilanes, polysilazanes, organopolysilanes, silsesquiazanes, carbon substituted polysilazanes, and polysilacyclobutasilazanes (ii) evaporating said solvent to thereby deposit a preceramic polymer precursor coating on said ceramic or ceramic-like coating; and (iii) ceramifying the preceramic polymer precursor coating by heating to a temperature between 200-900 DEG C. under an ammonia or inert gas atmosphere.

Alternatively, the passivating and/or barrier coating may be applied by the following methods. The silicon containing coating is applied by a means selected from the group consisting of (a) chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or mixtures thereof in an inert gas atmosphere, (b) plasma enhanced chemical vapor deposition a silane, halosilane, halodisilane, halopolysilane or mixtures thereof in an inert gas atmosphere and (c) metal assisted chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or mixture thereof in an inert gas atmosphere. The silicon carbon coating is applied by a means selected from the group consisting of (1) chemical vapor deposition in an inert gas atmosphere of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or mixtures thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane, (2) plasma enhanced chemical vapor deposition in an inert gas atmosphere of an alkylsilane, halosilane, halodisilane, halopolysilane or mixtures thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane and (3) plasma enhanced chemical vapor deposition of a silacyclobutane or disilacyclobutane in an inert gas atmosphere. The silicon nitrogen-containing coating is deposited by a means selected from the group consisting of (A) chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or mixtures thereof in an ammonia atmosphere, (B) plasma enhanced chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane, or mixtures thereof in an ammonia atmosphere and (C) ceramification of a silicon and nitrogen containing preceramic polymer precursor in the presence of ammonia or an inert gas atmosphere. The silicon carbon nitrogen-containing coating is deposited by a means selected from the group consisting of (i) chemical vapor deposition of hexamethyldisilazane in an ammonia or inert gas atmosphere, (ii) plasma enhanced chemical vapor deposition of hexamethyldisilazane in an ammonia or inert gas atmosphere, (iii) chemical vapor deposition of silane, alkylsilane, halosilane, halodisilane, halopolysilane or mixture thereof in the presence of an alkane of one to six carbon atoms or an

alkylsilane and further in the presence of ammonia, and (iv) plasma enhanced chemical vapor deposition of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or mixture thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane and further in the presence of ammonia.

Coatings produced by the instant invention possess low defect density and are useful on electronic devices as protective coatings, as corrosion resistant and abrasion resistant coatings, as temperature and moisture resistant coatings, as dielectric layers and as a diffusion barrier against ionic impurities such as sodium and chloride.

The following non-limiting examples are included so that one skilled in the art may more readily understand the invention.

#### EXAMPLE 1

Hydrogen silsesquioxane resin produced by the method of Frye et al. U.S. Pat. No. 3,615,272 issued Oct. 26, 1971, was diluted to 10 weight percent in an n-heptane solution containing 60 ppm platinum as platinum 2,4-pentanedionate. A 11/2 inch square copper thick film multilayer circuit board was coated with the solution and then spun at 3000 RPM for 35 seconds. The hydrogen silsesquioxane was then ceramified by placing the device in a 2 inch Lindburg furnace with an argon atmosphere, raising the temperature to 600 DEG C. and maintaining it for 1 hour. A coating approximately 2000 angstroms thick was produced thereby. FTIR spectra showed essentially no Si-H bonds.

#### EXAMPLE 2

This Example teaches the application of a second coating onto the coated copper thick film multilayer circuit board of Example 1. Said coated circuit board was coated with a second preceramic polymer solution of polycarbosilane diluted to 10 weight percent in n-heptane and then spun at 3000 RPM for 35 seconds. The coated substrate was then ceramified by placing the device in a 2 inch Lindburg furnace with an ammonia atmosphere, raising the temperature to 600 DEG C. and maintaining it for 1 hour. A ceramic coating approximately 2300 angstroms thick was thereby deposited.

#### EXAMPLE 3

Accuglas 305.TM., a preceramic polymer containing  $\text{MeSi(OH)}_x(\text{OEt})_y$  diluted to 10 weight percent in ethanol, was used to coat a 11/2 inch square copper thick film multilayer circuit board and the circuit board was then spun at 3000 RPM for 35 seconds. The Accuglas was ceramified by placing the device in a 2 inch Lindburg furnace with an argon atmosphere, raising the temperature to 700 DEG C. and maintaining it for 1 hour. A green ceramic coating 3296 angstroms thick was thereby deposited. FTIR spectra showed some methyl substitution but essentially no hydroxyl groups.

#### EXAMPLE 4

A solution of preceramic material was manufactured by mixing 4.5 g of  $\text{MeSi(OMe)}_3$ , 4.0 g of IPA, 0.4 g of acetic acid and 2.5 g of water and heating the resultant solution for 30 minutes at 60-70 DEG C. A 11/2 inch square copper thick film multilayer circuit board was coated with the solution and then spun at 3000 RPM for 35 seconds. The preceramic material was then ceramified by placing the device in a 2 inch Lindburg furnace with an argon atmosphere, raising the temperature to 700 DEG C. and maintaining it for 1 hour. A pink/gold ceramic coating 2682 angstroms thick was thereby deposited. FTIR spectra showed some methyl substitution but essentially no hydroxyl groups.

#### EXAMPLE 5

A solution of preceramic material was manufactured by mixing 5.04 cc of  $\text{Si}(\text{OEt})_4$ , 5.04 cc of ethanol, 9.92 cc of water and 2 drops of 5% HCl, heating the resultant solution for 30 minutes at 60-70 DEG C., and diluting the resultant solution to 3.3 weight percent solids with additional ethanol. A 1 1/2 inch square copper thick film multilayer circuit board was coated with the solution and then spun at 3000 RPM for 35 seconds. The preceramic material was then ceramified by placing the device in a 2 inch Lindburg furnace with an argon atmosphere, raising the temperature to 700 DEG C. and maintaining it for 1 hour. A blue/gold ceramic coating 3513 angstroms thick was thereby deposited. FTIR spectra showed essentially no hydroxyl substitution

What is claimed is:

1. A coated electronic device formed by a method consisting essentially of:  
(A) coating the electronic device with a solution consisting essentially of a solvent and hydrogen silsesquioxane resin;  
(B) evaporating the solvent to deposit a preceramic coating on the electronic device;  
(C) heating the preceramic coating to a temperature of between about 500 up to about 800 DEG C. under an inert gas atmosphere; and  
(D) applying a passivating coating over the coating of step (C), the passivating coating applied by means of (i) coating the electronic device having the coating of step (C) with a second solution comprising a solvent and a preceramic polymer, (ii) evaporating said solvent to thereby deposit a preceramic coating; and (iii) heating the preceramic coating to a temperature between 200-900 DEG C. under an ammonia or inert gas atmosphere, whereby a dual layer coating is obtained on the electronic device.

2. A coated electronic device formed by a method consisting essentially of:  
(A) coating the electronic device with a solution consisting essentially of a solvent and hydrogen silsesquioxane resin;  
(B) evaporating the solvent to deposit a preceramic coating on the electronic device;  
(C) heating the preceramic coating to a temperature of between about 500 up to about 800 DEG C. under an inert gas atmosphere;  
(D) applying a silicon containing passivating coating over the coating of step (C), said passivating coating selected from the group consisting of (i) silicon coatings, (ii) silicon carbon-containing coatings, (iii) silicon nitrogen-containing coatings, and (iv) silicon carbon nitrogen-containing coatings, wherein the silicon coating is applied by a means selected from the group consisting of (a) chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or mixtures thereof in an inert gas atmosphere, (b) plasma enhanced chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or mixtures thereof in an inert gas atmosphere and (c) metal assisted chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or a mixture thereof in the presence of an inert gas, and wherein the silicon carbon-containing coating is applied by a means selected from the group consisting of (1) chemical vapor deposition in an inert gas atmosphere of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or mixtures thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane, (2) plasma enhanced chemical vapor deposition in an inert gas atmosphere of an alkylsilane, halosilane, halodisilane, halopolysilane or mixtures thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane and (3) plasma enhanced chemical vapor deposition of a silacyclobutane or disilacyclobutane in an inert gas atmosphere; and wherein the silicon nitrogen containing coating is deposited by a means selected from the group consisting of (a') chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or mixtures thereof in an ammonia atmosphere, (b') plasma enhanced chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane, or mixtures thereof in an ammonia atmosphere and (c') coating the coating of step (C) with a second solution comprising a solvent and a preceramic polymer, evaporating said solvent to thereby deposit a preceramic coating and heating the preceramic coating to a temperature between 200-900 DEG C. under an ammonia or inert gas atmosphere, and wherein the silicon carbon nitrogen-containing coating is deposited by a means selected from the group consisting of (i) chemical vapor deposition of hexamethyl disilazane in an ammonia or

inert gas atmosphere, (ii) plasma enhanced chemical vapor deposition of hexamethyldisilazane in an ammonia or inert gas atmosphere, (iii) chemical vapor deposition of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or a mixture thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane and further in the presence of ammonia, and (iv) plasma enhanced chemical vapor deposition of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or a mixture thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane and further in the presence of ammonia, whereby a dual layer coating is obtained on the electronic device.

3. A coated electronic device formed by a method consisting essentially of:

(A) coating the electronic device with a solution consisting essentially of a solvent and hydrogen silsesquioxane resin;

(B) evaporating the solvent to deposit a preceramic coating on the electronic device;

(C) heating the preceramic coating to a temperature of between about 500 up to about 800 DEG C. under an inert gas atmosphere;

(D) applying a passivating coating over the coating of step (C), the passivating coating applied by means of (i) coating the electronic device having the coating of step (C) with a second solution comprising a solvent and a preceramic polymer, (ii) evaporating said solvent to thereby deposit a preceramic coating; and (iii) heating the preceramic coating to a temperature between 200-900 DEG C. under an ammonia or inert gas atmosphere; and

(E) applying a silicon containing barrier coating to said passivating coating, said barrier coating selected from the group consisting of (i) silicon coatings, (ii) silicon carbon-containing coatings, (iii) silicon nitrogen-containing coatings, and (iv) silicon carbon nitrogen-containing coatings, wherein the silicon coating is applied by a means selected from the group consisting of chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or mixtures thereof in an inert gas atmosphere, (b) plasma enhanced chemical vapor deposition of a silane, halosilane, halodisilane; halopolysilane or mixtures thereof in an inert gas atmosphere and (c) metal assisted chemical vapor deposition of asilane, halosilane, halodisilane, halopolysilane or a mixture thereof in the presence of an inert gas, and wherein the silicon carbon-containing coating is applied by a means selected from the group consisting of (1) chemical vapor deposition in an inert gas atmosphere of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or mixtures thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane, (2) plasma enhanced chemical vapor deposition in an inert gas atmosphere of an alkylsilane, halosilane, halodisilane, halopolysilane or mixtures thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane and (3) plasma enhanced chemical vapor deposition of a silacyclobutane or disilacyclobutane in an inert gas atmosphere; and wherein the silicon nitrogen containing coating is deposited by a means selected from the group consisting of (a') chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or mixtures thereof in an ammonia atmosphere, (b') plasma enhanced chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane, or mixtures thereof in an ammonia atmosphere and (c') coating the passivating coating with a third solution comprising a solvent and a preceramic polymer, evaporating said solvent to thereby deposit a preceramic coating and heating the preceramic coating to a temperature between 200-900 DEG C. under an ammonia or inert gas atmosphere, and wherein the silicon carbon nitrogen-containing coating is deposited by a means selected from the group consisting of (i) chemical vapor deposition of hexamethyl disilazane in an ammonia or inert gas atmosphere, (ii) plasma enhanced chemical vapor deposition of hexamethyldisilazane in an ammonia or inert gas atmosphere, (iii) deposition of a silane, alkylsilane, halosilane, halopolysilane or a mixture thereof in the presence one to six carbon atoms or an alkylsilane and presence of ammonia, and (iv) plasma enhanced deposition of a silane, alkylsilane, halosilane halopolysilane or a mixture thereof in the presence one to six carbon atoms or an alkylsilane and presence of ammonia, whereby a multilayer coating is obtained on the electronic device.

4. A coated electronic device formed by a method consisting essentially of:

(A) coating the electronic device with a solution consisting essentially of a solvent and hydrogen silsesquioxane resin;

(B) evaporating the solvent to deposit a preceramic coating on the electronic device;

(C) heating the preceramic coating to a temperature of between about 500 up to about 800 DEG C. under an inert gas atmosphere; (D) applying a silicon containing passivating coating to the coating of step (C), said passivating coating selected from the group consisting of (i) silicon carbon-containing coatings, (ii) silicon nitrogen-containing coatings, and (iii) silicon carbon nitrogen containing coatings, wherein the silicon carbon-containing coating is applied by a means selected from the group consisting of (1) chemical vapor deposition in an inert gas atmosphere of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or mixtures thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane, (2) plasma enhanced chemical vapor deposition in an inert gas atmosphere of an alkylsilane, halosilane, halodisilane, halopolysilane or mixtures thereof, in the presence of an alkane of one to six carbon atoms or an alkylsilane and (3) plasma enhanced chemical vapor deposition of a silacyclobutane or disilacyclobutane in an inert gas atmosphere; and wherein the silicon nitrogen containing coating is deposited by a means selected from the group consisting of (a') chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or mixtures thereof in an ammonia atmosphere, (b') plasma enhanced chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane, or mixtures thereof in an ammonia atmosphere and (c') coating the first coating with a second solution comprising a solvent and a preceramic polymer, evaporating said solvent to thereby deposit a preceramic coating and heating the preceramic coating to a temperature between 200-900 DEG C. under an ammonia or inert gas atmosphere, and wherein the silicon carbon nitrogen-containing coating is deposited by a means selected from the group consisting of (i) chemical vapor deposition of hexamethyldisilazane in an ammonia or inert gas atmosphere, (ii) plasma enhanced chemical vapor deposition of hexamethyl disilazane in an ammonia or inert gas atmosphere, (iii) chemical vapor deposition of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or a mixture thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane and further in the presence of ammonia, and (iv) plasma enhanced chemical vapor deposition of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or a mixture thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane and further in the presence of ammonia, to produce the silicon containing passivating coating; and (E) applying a silicon containing barrier coating to the passivating coating, the barrier coating selected from the group consisting of (i) silicon coatings, (ii) silicon carbon-containing coatings, (iii) silicon nitrogen-containing coatings, and (iv) silicon carbon nitrogen-containing coatings, wherein the silicon coating is applied by a means selected from the group consisting of (a) chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or mixtures thereof in an inert gas atmosphere, (b) plasma enhanced chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or mixtures thereof in an inert gas atmosphere and (c) metal assisted chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or a mixture thereof in the presence of an inert gas, and wherein the silicon carbon-containing coating is applied by a means selected from the group consisting of (1) chemical vapor deposition in an inert gas atmosphere of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or mixtures thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane, (2) plasma enhanced chemical vapor deposition in an inert gas atmosphere of an alkylsilane, halosilane, halodisilane, halopolysilane or mixtures thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane and (3) plasma enhanced chemical vapor deposition of a silacyclobutane or disilacyclobutane in an inert gas atmosphere; and wherein the silicon nitrogen-containing coating is deposited by--a means selected from the group consisting of (a') chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane or mixtures thereof in an ammonia atmosphere, (b') plasma enhanced chemical vapor deposition of a silane, halosilane, halodisilane, halopolysilane, or mixtures thereof in an ammonia atmosphere and (c') coating the passivating coating with a second solution comprising a solvent and a preceramic polymer, evaporating said solvent to thereby deposit a preceramic coating and heating the preceramic coating to a temperature between 200-900 DEG C. under an ammonia or inert gas atmosphere, and wherein the silicon carbon nitrogen-containing coating is deposited by a means selected from the group consisting of (i) chemical vapor deposition of hexamethyldisilazane in an ammonia or inert gas atmosphere, (ii) plasma enhanced chemical vapor deposition of hexamethyldisilazane in an ammonia or inert gas atmosphere, (iii) chemical vapor deposition of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or a mixture thereof in the presence of an alkane of one to

six carbon atoms or an alkylsilane and further in the presence of ammonia, and (iv) plasma enhanced chemical vapor deposition of a silane, alkylsilane, halosilane, halodisilane, halopolysilane or a mixture thereof in the presence of an alkane of one to six carbon atoms or an alkylsilane and further in the presence of ammonia, whereby a multilayer coating is obtained on the electronic device.

## **Glass article having a durable water repellent surface**

### **Glass article having a durable water repellent surface**

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Inventor(s):

HAN JOO HUN (KR); HONG BYUNG SUN (KR)

Applicant(s):

SAMSUNG CORNING CO LTD (US)

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### **Abstract**

A glass substrate is provided with a durable and abrasion-resistant water-repellent surface, by

coating a surface of the substrate with a silica solution which has been subjected to a two-step aging process, respectively in the presence of basic and acidic catalysts, which is then thermally treated to provide a coarse-surfaced silica layer including fine crystalline silica particles, which is then coated with a water-repellent layer made of fluoroalkylsilane

## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

This invention relates to a glass article having a water repellent surface having excellent durability. In particular, a coarse surface silica layer having micro-crystal silica particles is formed on the glass substrate. On top of a surface, fluoroalkylsilane (FAS) is applied, forming such water-repellent layer. More particularly, this invention relates to such water-repellent glass having a superior durability and water repellent property, and to a process for manufacturing the same, in which long-term use does not induce deformation in appearance and deterioration in water-repellent property.

### 2. Background of the Invention

In the case of various types of glasses exposed to an external environment, such as safety glass windows for automobiles, building glass windows, and mirrors, the surface of such glass articles frequently becomes contaminated with rain or some other moisture resulting in a poor visual field. In order to solve that problem, a water-repellent property conventionally has been added to the surfaces of such glass articles.

In general, to provide a water-repellent property to the surface of a glass article, the surface energy at the glass surface should be lowered. To this end, a substance having low surface energy (hereinafter referred to as "water-repellent agent") should be placed on the glass surface. In line with this, a common type of soda lime glass plate shows a contact angle of about 20 DEG to water, but a glass sample with excellent water-repellent treatment shows a contact angle of more than 100 DEG.

As prior art, "RAIN-X" (Unelko Corp. USA, U.S. Pat. No. 3,579,540), the currently commercialized process for coating a silicon-based water repellent agents, for such uses is the most well known process via-a-vis adding a water-repellent property to the surface of a glass substrate via coating a with a water-repellent agent. In general, hydrocarbon-based, silicon-based, chlorine, or fluorine compounds are being used as water-repellent agents, for such uses. Among them, hydrocarbon- and silicon-based compounds have a critical surface tension of about 30 dyn/cm, and fluorated alkyl compounds (hereinafter referred to as "Rf compounds") containing CF<sub>3</sub> and CF<sub>2</sub> groups within the on the surface of the glass substrate that is to be made water repellent tension of less than 20 dyn/cm, thus effectively repelling water, polar solvent, and even oil.

Hitherto, the fluoroalkylsilane-based water-repellent agents have been reported as having the best water-repellent property among the conventional water-repellent agents since they have an ample amount of CF<sub>3</sub> or CF<sub>2</sub>, a substance providing the lowest surface energy. Further, the corresponding linear structure is quite advantageous in increasing the density of water-repellent group.

A water-repellent agent for, providing the water-repellent property to glass, has a molecular site with tendency to induce a strong siloxane bond (Si--O--Si) by reacting with a silanol (OH) group at the glass surface and an Rf group with a fluorocarbon group providing a hydrophobic property at the other side contacting air. With such structural characteristics, various methods of providing a water-repellent property on a glass surface using Rf compounds have been developed as the

most practical approach. However, in the case where these fluorine compounds are applied to soda lime glass, the dissolution of alkali within the glass is responsible for degrading the water-repellent property, with the passage of time.

Therefore, it is necessary that a fine and firm silica film be coated on the surface of the glass substrate that is to be made water repellent, prior to the water-repellent film, in conjunction with inhibiting the dissolution of alkali substances within the glass. In particular, in the case of the automobile glass which is vulnerable to the external environment due to ceaseless surface friction and contamination, its water-repellent capability from the direct treatment by water-repellent agent is insufficient. Thus, additional factors for durability should also be considered. Durability as applied here means resistance from abrasion, scratching, rain, wind, chemical substances, sun rays, ultraviolet and temperature, etc. Namely, such durability allows the continuation of the water-repellent property for a long period of time, for the enjoyment of the functional benefits of the water-repellent glass.

In the past, many inventors have extended their intensive studies to improve the durability of water-repellent glass in various aspects. Among the conventional methods, for the purpose of providing durability to the water-repellent film, the technology of forming a sub-layer film, comprising highly adhesive and durable materials, at the surface of the desired substrate prior to forming a water-repellent film has been in common usage in the field of coating technology, using the sol-gel method. Namely, it is a method of double film treatment in which a silica layer using tetraethoxysilane (TEOS) is first formed at the surface of the glass substrate, and then, a water-repellent film comprising an Rf compound is formed thereon. In addition to TEOS, other metal oxides such as  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{ZnO}_2$  or ITO may be selected use as the silane compound.

However, if the water-repellent agent is directly applied to the plain glass and the silica surface, the adhesion area to the slippery surface is relatively small. Thus, easy removability of the water-repellent agent from the surface cannot sustain the durability and water-repellent property.

To solve this problem, the Japanese Unexamined Patent Applications Hei No. 4-325446 and Hei No. 5-24885 disclose methods of enhancing the durability in such a manner to form fine pores within a silica layer, by mixing polyethylene glycol and triethylene glycol monoethylene ether when forming the silica layer. Further, the Japanese Unexamined Patent Applications Hei No. 4-124047 and Hei No. 6-116430 disclose methods of forming at least one transparent metal oxide layer at the glass surface and a modifying the surface thereafter via wet etching or plasma discharge etching, and then finally forming the water-repellent layer on the of the surface as so modified.

However, the fine pores within the silica layer formed by the methods of the Japanese Unexamined Patent Applications Hei No. 4-325446 and Hei No. 5-24885 are not stable during thermal treatment process at temperature of more than 400 DEG C., thereby unduly restricting the thermal treatment process. Furthermore, the methods disclosed by the Japanese Unexamined Patent Applications Hei No. 4-124047 and Hei No. 6-116430 have the disadvantage of requiring an additional etching process after the formation of the silica layer.

Meanwhile, the Japanese Unexamined Patent Application Hei No. 5-147976 discloses a metal oxide manufacturing method which provides an ample amount of fine coarse surface via the sol-gel method, using a sol-gel which is prepared from and obtained by mixing two sols having different molecular weights, and using metalalkoxide or methylacetylacetonate.

Nevertheless, such methods have disadvantages and require improvement in that a) the durability effect which they provide is not satisfactory, and b) the processes are complicated so that there a small economic benefits.

#### SUMMARY OF THE INVENTION



The objective of the invention disclosed herein is to provide the surface of a glass substrate with a water-repellent characteristic with superior durability, including abrasion resistance, which will solve the above-mentioned problems. In the process of forming a silica layer comprising metal oxides at the surface of a conventional glass, substrate the fine granular silica crystal particles are evenly distributed within such film. Then, by thermal treatment at low temperature, the water-repellent layer is formed on the silica layer. Henceforth, in a more economical and efficient manner, such film water-repellent surface treatment which is applied to a glass according to the invention which is disclosed herein effectively prevents deterioration of functional aspects and deformation of the external appearance of the glass substrate.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is the diagram showing in cross section the structure of the durable water-repellent glass article according to this invention.

FIG. 2 is the photograph of transmission electron microscopy (1.times.10@5 times enlargement) showing a cross section of the silica layer formed after by coating the glass surface with silica solution during the process of preparing the durable water-repellent glass article of this invention.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

This invention is explained in more detail hereunder by way of example, with reference to the accompanying drawings.

The durably water-repellent glass substrate of this invention is characterized in that a durable silica layer 2, comprising a silica compound, is formed at the surface of the glass substrate 1. In particular, an ample amount of fine silica crystal particles 4 are distributed within the silica layer 2.

As illustrated in the cross-sectional diagram of FIG. 1, the water-repellent glass, has a silica layer 2 is formed at the surface of the glass substrate 1 for the purposes of providing durability to the same. On the silica layer 2, fluoroalkylsilane (FAS) is applied, forming the water-repellent layer 3. In order to enhance durability including abrasion resistance of the silica layer 2 and the water-repellent layer 3, the fine granular silica crystal particles 4 are distributed within the silica layer 2.

According to this invention, the formation of the silica crystal particles 4 is due to the fact that an aging process is provided as a two-step process during the making of the silica sol comprising the silica layer 2. Consequently, an ample amount of fine silica crystal particles 4 are generated within the the layer 2, so that the mechanical properties, including abrasion resistance of the glass are enhanced. The silica crystal particles, so formed, are of a granular type, and some which are hollow may be formed.

The silica layer 2 is formed from a silica solution, which is subjected to the two-step aging process, and as a result of a thermal treatment of the substrate, surface coarseness is provided on the silica layer 2.

A process for preparing the water-repellent glass substrate of this invention is explained in more detail hereunder.

The process for preparing the water-repellent glass substrate having a silica layer at the surface of the glass substrate is as follows: As for the silica solution a metal alkoxide-based silane compound is subjected to a two-step aging process for the manufacture of a silica solution in which two polymers are cross-linked. Then, the surface of the glass substrate is coated with this solution, after which the substrate undergoes thermal treatment for the formation of the silica layer having surface coarseness. Thereafter, the surface of the silica layer having surface coarseness is coated with the water-repellent agent, for the formation of the water-repellent layer.

According to this invention, in order that the silica sol solution for preparing the silica layer will have a cross-linked structure where granular colloid silica solution and linear polysiloxane solution are mixed, the silica sol solution is subjected to a first step of the aging process in the presence of a basic catalyst, and then to a second step of the aging process in the presence of acidic catalyst. Such procedure is designed to provide surface coarseness to the silica layer and to distribute fine silica crystal particles in the film after a thermal treatment. The silica solution is formed by adding a solvent (e.g., ethanol) to tetraethoxysilane (TEOS). Further, in order to facilitate hydrolysis, distilled water ( $H_2O$ ) is used. Aqueous ammonia solution ( $NH_4OH$ ) may be selected as a basic catalyst used for the first step of the aging process, and hydrochloric acid ( $HCl$ ) may be selected as an acidic catalyst used for the second step of the aging process.

Further, according to this invention, a thermal curing process should be performed for the preparation of the silica layer using the second step aged silica solution. It is preferred that a small amount of inorganic salt be added to the silica solution for the purposes of lowering the thermal curing temperature. It is advantageous to use the inorganic salt in aqueous solution in mixing. Also, it is preferred to use such inorganic salt in the amount of 0.1.about.3.0 wt % to water. The inorganic salts used for this reaction include  $NaCl$ ,  $NH_4Cl$ ,  $KNO_3$ ,  $NaNO_3$ , or  $CH_3COONa$ , but it is particularly preferred to use  $KNO_3$ .

According to this invention, the first step of the aging process of the silica solution is performed in such a manner that tetraethoxysilane is added to the solvent, for mixing and stirring at room temperature. With the addition of basic catalyst, the reacting solution is stirred until the pH is more than 9.0. Then, the first step of the aging is carried out at room temperature 80 DEG C. for 12.about.24 hours. If the first-step aging time is longer than 24 hours, the poor water-repellent durability results, due to the fact that excessive development of granular particles (granular silica crystal particles) prevents the formation of the required structural density. Meanwhile, if the amount of basic catalyst used for the first aging is more than 1 wt % in proportion to the silica solution, opaqueness in the coating may occur. Thus, it is preferred to use less than 1 wt % of basic catalyst. By hydrolysis and polycondensation associated with the first aging in the presence of basic catalyst colloidal silica which is granular silica polymer is formed due to the nucleophilic condition of Si. In the process of such reaction, the second aging is performed, with the addition of acidic catalyst and water, for more than 2 hours, until the pH becomes approximately 1.2.about.2.7. Then, unhydrolyzed  $Si(OR)_4$  is subjected to hydrolysis and polymerization, thus effectuating the shape of polysiloxane, which is a linear polymer, by electrophilic attack. Consequently, the sol formed via the second step of the aging process will have a crosslinking form where both granular and linear polymers coexist. Based on such morphological characteristics, the second-step aged silica solution is coated at the surface of the glass and thermally treated. As a result, coarseness at the glass surface may be naturally formed without any separate process.

According to this invention, coating with the silica solution may be made by dipping or spraying. In addition to these methods, some well-known coating methods may also be applied. If the dipping method is used a substrate made of soda lime glass of 2.5.times.7 cm, in proper size, is immersed in silica sol solution, formed by the above-described two-step aging process, so as to naturally form a coating film, with slow raising of the glass substrate being coated, from the silica sol solution.

The preferred raising speed is in the range of 10.about.30 cm per minute. If the speed is fast, an increased thickness of the coating film results, which is responsible for non-homogeneous of the film and poor glass transparency. However, if such raising speed is too slow, the extremely thin film thereby formed cannot have sufficient durability.

Alternatively, if the spray-coating method is used, the silica sol is sprayed onto a soda lime glass substrate of 30.times.30 cm size. Special caution in spraying should be exercised. The thickness of the coating film increases if too much of a volume is sprayed and the distance between nozzle and specimen is too close. Under the spray method for coating the total specimen area, the

nozzle is first moved from the left to right, and then the nozzle is lowered by approximately 3 cm, after which the nozzle is moved from the right to left, and so on. However, in the process of moving the nozzle, some areas of the specimen are sprayed-onto a second time. The poor appearance in such areas becomes more severe at low temperature or humidity, but under the condition of 50% humidity or more, especially 80% humidity or more, appearance defects at the borders where spray passes overlap will not occur.

When the silica solution is applied onto the glass surface using either procedure described above, it is preferred that the thickness of the coating film be in the range of 600.about.1500 .ANG., more preferably in the range of 600.about.1000 .ANG.. If the coating film is extremely thin, there will be insufficient durability improvement. Further, if the coating film extremely thick, the film will be non-homogeneous and poor in quality.

After the glass substrate surface has been coated with the silica sol solution the thus coated article undergoes thermal treatment at a temperature of 180.about.550 DEG C., preferably at a temperature of 180.about.350 DEG C. for more than 30 minutes. If the thermal treatment temperature is higher than 550 DEG C., this does not affect the water-repellent property regarding the change in the first-step aging time in the presence of basic catalyst. However, in the case of the second-step aging time in the presence of acidic catalyst, there will be a significant reduction in the water-repellent power after 3 days from manufacture. Also, if the thermal treatment temperature is lower than 180 DEG C., the density and hardness of the film will deteriorate. Meanwhile, according to this invention, when the silica sol, which has been seen subjected to a one-day first step of the aging process with the addition of  $\text{NH}_4\text{OH}$  as basic catalyst, and to a second-step of the aging process with the addition of  $\text{HCl}$  as acidic catalyst and the resultingly coated article undergoes a thermal treatment at approximately 200.about.300 DEG C., the water-repellent durability of the resulting coating proves to be superior to that of an otherwise similarly manufactured coated glass substrate which has been produced at a higher temperature.

Through the above described thermal treatment, the silica forms the siloxane cross-linking layer of strong  $\text{Si-O-Si}$  bonds to the glass.

FIG. 2 is a photograph showing by transmission electron microscopy, a cross section of the silica layer, as formed on the surface of the glass aforementioned. Referring to FIG. 2, it is ascertained that the film thickness of the silica layer is in the range of 650.about.1500 .ANG. depending on the solution and coating condition, and fine granular silica crystal particles are evenly distributed within the silica layer. It is ascertained that the particles of FIG. 2 are silica crystal particles when analyzed by X-ray diffraction pattern. The diameters of such particles are in the range of 100.about.300 .ANG., and they are of a granular type, with a hollow or filled inner part. In general, it appears that they are in the silica matrix phase, amorphous and in a chemically coherent state.

According to this invention, if such silica crystal particles, which are coherently bordered with the silica matrix, are diffused as shown in FIG. 2, the induced effect, such as combining material thereto, may enhance the mechanical properties, including durability of the film, and including the resistance to abrasion, in particular. Since the production of such particles is derived from chemical and thermodynamic reaction, this may be achieved via the manufacture of the silica sol solution based on the two-step aging process of this invention.

A commonly available water-repellent solution may be used for coating the silica layer formed on the surface of the glass substrate according to this invention. For example, fluoromethoxysilane ( $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ ), isopropyl alcohol, hydrochloric acid ( $\text{HCl}$ ) and distilled water are blended in a certain chemical ratio and the blend is subjected to hydrolysis for a certain time prior to use.  $\text{HCl}$  or a similar acid is used for the catalyst to facilitate the hydrolysis, and isopropyl alcohol is added as a solvent. The reason why the water-repellent agent is under hydrolysis and polycondensation is to maximize the siloxane reaction ( $\text{Si-O-Si}$ ) by facilitating the reaction between the  $\text{Rf}$  group and silanol group ( $\text{OH}$ ) at the surface of the silica layer.

According to this invention, some Rf compounds which can be used in constituting water-repellent agent solution include  $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{SiCH}_3(\text{Cl})_2$ ,  $\text{CF}_3\text{CH}_2\text{CH}_2\text{SiCl}_3$  and  $\text{CF}_3\text{CH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$ , in addition to fluoromethylsilane ( $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ ). Further, nitric acid and acetic acid can be used as a catalyst, in addition to hydrochloric acid being able to be used.

The water-repellent coating based on the water-repellent agent solution, may be applied under the same conditions as the coating for formation of the silica layer. Then, if the glass substrate coated with water-repellent agent is heated and dried at 120.about.170 DEG C. for more than 30 minutes, the water-repellent layer will thus be formed.

It has been reported that the contact angle of a water drop, a criterion of the water-repellent property on the durable water-repellent glass having such a water-repellent layer, is a function of the coarseness characteristics of the Rf group, the chemical composition of the water-repellent agent, and its surface shape (New Glass Vol. 12 No. 2, 1996). Namely, it means that the contact angle may increase depending on the coarseness surface.

In addition to that, the further coarseness of the silica layer increases the surface area, and a more durable water-repellent layer is formed by increasing the chemical reaction sites with the water-repellent agent, such as by providing a silanol group at the surface. Thus, the durability may be improved even under such severe condition of wear and tear.

This invention is further explained based on the following examples in more detail.

#### EXAMPLE 1

##### Preparation of Water-repellent Glass Based on Two-step Aging Process of Silica Solution and Dip-coating Method

###### A. Synthesis of silica layer-former solution

A mixture of 52 g of tetraethoxysilane (TEOS) and 448 g of ethanol was stirred for 30 minutes, and with the addition of 2.5 g of  $\text{NH}_4\text{OH}$ , the reacting solution was further stirred for 1 hour. Then, 16 g of 1 wt %  $\text{KNO}_3$  aqueous solution was added to the reacting solution, stirred for 2 hours, tightly closed and subjected to aging in a thermostatic bath at 30 DEG C. for 24 hours.

5 g of hydrochloric acid was added to the solution, stirred for 2 hours. Then, the synthesis of the silica layer-forming solution was completed.

###### B. Preparation of silica layer

A sheet soda lime glass was cut provide a piece measuring 2.5.times.7 cm (thickness: 0.1 cm) and that piece was subjected to a first washing, using a surfactant. After dipping the piece of glass in distilled water, the piece of glass was subjected to a second washing for 15 minutes, using an ultrasonic cleaner. Then, the piece of glass was subjected to a third washing, using acetone, and dried with a dryer at 120 DEG C. The specimen was then immersed in a silica layer-forming silica sol solution for 30 seconds, using a motor driven dip coater and increasing the speed to a rate of 11 cm/min. The sample was under thermal treatment at 300 DEG C. with the temperature increasing at a rate of 7 DEG C./min.

###### C. Preparation of water-repellent layer

A water-repellent coating was provided on the glass substrate having the silica layer. For that purpose, fluoromethylsilane ( $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ ), ethanol, hydrochloric acid and distilled water as starting materials for making a water-repellent solution were mixed in a

respective ratio of 3 g, 150 g, 1 g and 0.3 g. Then, the mixture was stirred at room temperature for 5 hours and subjected to aging for 1 day. The sample having the silica layer was coated using the water repellent agent under the same condition as are above, using the dip coater. The sample coated with the water-repellent agent was heated and dried at 150 DEG C. for 1 hour for the formation of the water-repellent layer.

#### D. Assessment and analysis of various physical properties

The contact angle on the glass sample formed with the above described silica layer and water-repellent layer was measured, together with abrasion/alkali resistance, anti-acidity and heat-resisting property. The contact angle was measured by the method of sessile drop using the contact angle instrument (model CA-X, Kyowa Interface Science Co. Ltd.). After measuring the contact angle 5 times at different places, the mean value was calculated.

The abrasion-resistance was measured in such a manner that an automotive wiper blade was cut to a 1 cm size in length. With a load of 300 g/cm given to the wiper blade piece on the glass sample was subjected to double-trip test 5000 times at a double-trip rate of about 2 seconds and then, the contact angle was measured for assessment.

An alkali-resistance test was performed in such manner that the specimen was quenched in 1N NaOH solution for 6 hours and taken out for the measurement of the contact angle. An anti-acidity test was performed in such manner that the specimen was dipped in 1N HCl solution for 6 hours and taken out for the measurement of the contact angle.

The heat resistance property was assessed in such a manner that the specimen was dipped in boiling water for 2 hours and taken out for the measurement of the contact angle, particularly reduction of the contact angle.

With reference to the abrasion resistance and visual haze, the visual haze (KS L 2007 standard test method) was assessed by Hazemeter (BYK Gardner, Germany) after rotating the sample 100.about.500 times using the Taber abrasion device (5150 Taber Abraser, USA).

Meanwhile, with reference to the surface coarseness of the coated glass, its Ra (centerline average, centerline mean coarseness) value, a criterion of the surface shape and surface coarseness, was calculated using the Atomic Force Microscopy (AFM)(DI 3000, USA).

Further, transmission electron microscopy was used for observation of the coated cross section.

The above measurements and observed results are shown in the the accompanying Tables 1 and 2.

#### EXAMPLE 2

##### Preparation of Water-repellent Glass Based on Two-step Aging Process of Silica Solution and Spray-coating Method

The manufacture and assessment of silica sol solution, including subjection the second-aging designed for the formation of a silica layer, was made performed as described above in relation to Example.

In an effort to make a coating on a glass substrate, using the silica sol solution which has undergone the two step aging process, the glass substrate having 30.times.30 cm in size was washed. The distance between the spray nozzle and specimen was 15 cm, and the moving speed of nozzle was 40 cm/sec. The coating was made at room temperature under an atmosphere of 85% humidity, and the air pressure and solution pressure for injection were adjusted to be 0.7 bar and 0.5 bar, respectively. The spray coating for the total specimen area

was performed in the following manner: After the nozzle was moved at 40 cm/sec from the upper left part of specimen to right, it was moved downward by 3 cm. Thereafter, the nozzle was moved from right to left at the same speed as above, and it was again moved downward by 3 cm, and so forth. Then, the spray-coated glass was subjected to thermal treatment at 300 DEG C. for 30 minutes, at an increasing temperature rate of 7 DEG C./min. The thickness of the silica layer formed by this process is 850 .ANG..

By the same procedure as described in Example 1, the silica layer-formed sample was coated with the water-repellent agent for the formation of the water-repellent layer.

The assessment of various physical properties relating to the water-repellent glass, so prepared, is shown in the accompanying tables 1 and 2.

## COMPARATIVE EXAMPLES 1 AND 2

### Preparation of Water-repellent Glass Using Polysiloxane-structure Silica Sol

A mixture of TEOS, ethanol, distilled water and catalytic hydrochloric acid in respective blending ratio of 72.8 g, 601.9 g, 25.2 g and 0.14 g was added to the silica-forming solution and stirred at room temperature for 3 hours. The reacting solution was again subjected to an aging process at room temperature for 4 days to obtain polysiloxane-structure silica sol solution. The water-repellent glass so prepared by such method, was assessed by the same procedure as Example 1. Each silica layer-formed specimen was prepared by dip coating method (comparative Example 1) and spray coating method (comparative Example 2). The formation of the water-repellent layer was also made available by the same procedure as the Example 1.

An assessment of various physical properties relating to the water-repellent glass, so prepared, is shown in the accompanying Tables 1 and 2.

TABLE 1

Comparison of Initial Contact Angle, Water-repellent Durability and Fundamental Properties

Example Comparative Example

Classification 1 2 1 2

Appearance Excellent Excellent Excellent Excellent

Fine Particles Presence Presence Absence Absence

Surface Coarseness 42 110 15 19

(Ra, .ANG.)

Initial Contact Angle 122 123 106 105

Anti-abrasiveness 108 109 98 97

(Wiper Blade Method)

Acid Resistance 118 119 102 102

Alkali Resistance 109 108 97 96

Heat Resistance 119 118 105 103

As revealed in Table 1, no diffused crystal particles in the silica layer were observed from the comparative Examples 1 and 2.

TABLE 2

Assessment of Contact Angle and Visual Haze after TABER Abrasion Test

Assessment of Contact angle and Haze after Taber Abrasion Test

(100.about.500 times)

100 Times 300 Times 500 Times

Contact Haze Contact Haze Contact Haze

	Angle ( DEG )	(.DELTA. H %)	Angle ( DEG )	(.DELTA. H %)
Example 1	104	0.6	98	0.7
2	106	0.5	99	0.7
Comparative 1	97	0.7	87	0.8
Example 2	95	0.7	85	0.8

As can be seen from Table 1, various physical properties of the test samples (e.g., initial contact angle and water-repellent durability) show that the water-repellent glass based on the silica layer, so prepared by the two-step aging method from Example 1 and 2, has proven to be superior to that of comparative Examples 1 and 2, which were prepared so as to have a conventional simple silica layer, in terms of water-repellent durability including anti-abrasiveness as well as initial contact angle. Further, the fact that both Examples 1 and 2 have a high value of more than 120 as an initial contact angle is due to the coarse surface of the water-repellent glass.

With reference to the above, the photograph of atomic force microscopy (AFM) of FIG. 2 shows the surface coarseness of the sample prepared by Example 1, its Ra value was about 42 .ANG.. Meanwhile, from the test of anti-abrasiveness and alkali-resistance measured by the wiper blade method described above, it was revealed the values for the water-repellent glass made by the method of two-step aging was higher than that of simple silica film of the comparative Examples by more than 10 DEG .

Table 2 shows the measurement results of the contact angle and visual haze value after the Taber abrasion test. Both Examples 1 and 2 maintained a water-repellent power of more than 90 DEG by 500 times, while the simple silica film had the contact angle of less than 90 DEG by 300 times, but its contact angle was reduced to less than 80 DEG by 500 times. Further, from the measurement of visual haze, all samples showed excellent water-repellent powder having less than 2.0% of .DELTA.H. In particular, less than 1.0% from both Examples 1 and 2 was observed in the change of haze value by 500 times. Further, since the change of haze on Taber abrasion was negligible, the durability of both Examples 1 and 2 was greatly improved.

As aforementioned, according to the invention disclosed herein, various glass substrates, such as safety glass for the windows of an automobile, building glazing, and mirrors, for the purposes of giving durability, are coated with silica solution which has been subjected to a two-step aging process in the presence of basic and acidic catalysts. As a result, a coarse surface silica sub-layer having micro-crystal silica particles is formed on the glass substrate. On top of such surface, fluoroalkylsilane (FAS) is applied, forming a water-repellent layer. The water-repellent glass so prepared in accordance with principles of the present invention has excellent water-repellent property and better durability including abrasion-resistance than that prepared using conventional methods. Its long-term use does not induce deformation in appearance nor deterioration in water-repellent property.

In particular, the process of manufacturing the water-repellent glass in accordance with principles of the present invention proves to be quite effective for providing superior durability to the glass in a simpler and more economic manner than the conventional method. The silica layer, formed by means of the silica solution which has undergone the two-step aging process in the presence of basic and acidic catalysts for the purpose of providing durability, has naturally an ample amount of micro crystal silica particles with the formation of the surface coarseness.

As set forth above, the invention herein relates to water-repellent glass having superior durability and water-repellent property, and the process for manufacturing the same, in which long-term use does not induce deformation in appearance and deterioration in water-repellent property.

What is claimed is:

1. An article having a water-repellent surface, comprising:

a glass substrate having a surface;  
a layer of a silica composition formed on said surface of said glass substrate, said silica composition including silica crystal particles evenly distributed within said layer and present at a surface of said layer of silica composition presented away from said surface of said glass substrate; and  
a layer of water-repellent film formed on said layer of silica composition, and  
wherein said layer of silica composition is formed by:  
subjecting a tetraethoxysilane solution to a first aging step under one of basic and acidic conditions, and then to a second aging step under the other of acidic and basic conditions;  
coating said surface of said glass substrate with said solution, so aged; and  
subjecting said glass substrate as coated by said solution to a thermal treatment.

2. The article of claim 1, wherein:  
said layer of silica composition has a thickness in the range of 600-1000 .ANG..

3. The article of claim 1, wherein:  
as a result of said thermal treatment, said layer of silica composition comprises a polymer of granular colloidal silica cross-linked with a linear polymer of polysiloxane.

4. The article of claim 1, wherein:  
at least some of said silica crystal particles are hollow.

5. The article of claim 1 or 4, wherein:  
said silica crystal particles range in size from 100 to about 300 .ANG. in diameter.

## **Ultra thin zircon coating and membrane.**

## **Ultra thin zircon coating and membrane.**

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Inventor(s):  
LETURE MARCEL P J A (FR); DAUGER A (FR); PRASSAS MICHEL (FR)

Applicant(s):  
CORNING INC (US)

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### Abstract

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A process to synthesize zircon as an ultra thin coating and comprising: (A) mixing an alcoholic sol resulting from hydrolysis of a silicon alkoxide with an alcoholic solution of a chelated zirconium compound and in the presence of and with a doping agent, until a homogenous mixed sol is obtained; (B) forming a matured sol containing colloidal particles and/or the polymeric entities from the mixed sol; (C) forming a coating of the matured sol on a microporous substrate; (D) drying slowly the sol coating into a gel coating free of flaws; and (E) firing the gel coating at a temperature of 900 to 1500 DEG C to form an ultra thin zircon layer. Use of the zircon layer obtained above as an ultrafiltration membrane or as a protective coating.

## Method for providing a metal surface with a vitreous layer

### Method for providing a metal surface with a vitreous layer

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Inventor(s):  
JONSCHKER GERHARD (DE); MENNIG MARTIN (DE); SCHMIDT HELMUT (DE)

Applicant(s):  
INST NEUE MAT GEMEIN GMBH (DE)

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### Abstract

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PCT No. PCT/EP98/02076 Sec. 371 Date Oct. 8, 1999 Sec. 102(e) Date Oct. 8, 1999 PCT Filed Apr. 9, 1998 PCT Pub. No. WO98/45502 PCT Pub. Date Oct. 15, 1998 Disclosed is a process for providing a metallic surface with a vitreous layer which is both decorative and scratch resistant and corrosion inhibiting. Said process is characterized in that a coating composition which is obtainable by a process comprising the hydrolysis and polycondensation of one or more silanes of the general formula (I)  $R_nSiX_{4-n}(I)$  wherein the groups X, the same or different from each other, are hydrolyzable groups or hydroxyl groups, the radicals R, the same or different from each other, represent hydrogen, alkyl, alkenyl or alkynyl groups having up to 12 carbon atoms and aryl, aralkyl and alkaryl groups having 6 to 10 carbon atoms, and n is 0, 1 or 2, provided that at least one silane with n=1 or 2 is employed, or oligomers derived therefrom, in the presence of a) nanoscaled SiO<sub>2</sub> particles and/or b) at least one compound selected from the group consisting of the oxides and hydroxides of the alkali and alkaline earth metals; is applied onto said metallic surface and the resulting coating is thermally densified to form a vitreous layer.

The present invention relates to a process for providing a metallic surface with a vitreous layer.

Vitreous layers on e.g. steel are generally produced by enamelling processes. For said purpose an adhesive layer is applied thereon, followed by, via a suspension (engobe), a particle-containing composition which upon heating melts to form a glass. Usually said composition is a lead containing glass system (in order to lower the melting point) which is characterized by a relatively high alkali content which serves to match the expansion coefficient of the glass with that of the steel. However, said procedure entails the disadvantage that the resulting enamel layers are usually not completely satisfactory as regards their chemical resistance. In order to obtain closed dense layers, the layer thickness must usually be above 50  $\mu m$ . This makes the layers inflexible and brittle and thereby sensitive to bending, impact and shock (they chip off). Another method is the electrodeposition of chromium oxide interference layers. However, said layers are not scratch resistant and are very sensitive with respect to staining and fingerprints due to their coloring interference effect.

Numerous studies have been conducted as regards the application of thin layers on steel surfaces by means of sol gel techniques. For example, it has been tried to provide stainless steel surfaces with zirconium dioxide layers in order to improve corrosion resistance. Borosilicate glass layers have also been studied. However, it was found that the refractory systems (high melting

oxides such as  $ZrO_2$ ) do not result in dense layers via said techniques and that the borosilicate glass layers could only be applied in layer thicknesses of significantly below 1  $\mu m$  so that a sufficient mechanical and chemical protection could not be secured.

According to the present invention it has now been found that by using specific, organically modified systems based on  $SiO_2$  vitreous layers can be formed on metallic surfaces, which layers may be as thick as 10  $\mu m$  without occurrence of cracking upon drying and densification thereof. Said effect is attributed to the improved relaxation behaviour of the organically modified silica gel and silica, respectively, skeletons. Surprisingly it has also been found that such layers can be converted into dense  $SiO_2$  films (for example on stainless steel or steel surfaces) already at relatively low temperatures (generally starting from 400 DEG C.). Such films are usually 3 to 5  $\mu m$  in thickness and form a hermetically sealing layer which prevents or drastically reduces, respectively, the access of oxygen to the metallic surface and secures an excellent protection against corrosion even at elevated temperatures. Such layers are furthermore abrasion resistant so that they can for example be rubbed with steelwool on the surface thereof without leaving any trace. After 100 cycles of Taber-Abrader-test (CS-10F, 500 g) they also show only hardly visible traces. Furthermore they are flexible, i.e., bending or folding the surface does not result in any cracks or other deterioration of the layers.

Additionally, the layers are usually clear as glass and transparent and may be applied in a manner such that the metallic surface will not be changed in its appearance. For example, it is possible to apply such layers on construction parts made of stainless steel without occurrence of a change in appearance.

Finally, further, already known colored vitreous layers, for example thin colloid-colored vitreous layers, may be provided on such vitreous layers. Since such colored vitreous layers are preferably prepared by means of coating compositions containing, for example, metal colloid precursors it may thereby be prevented that the metallic surface (or the metal ions released therefrom, respectively) (adversely) affect the reactions of the metal colloid precursors etc., since there will be no direct contact between the metallic surface and the colored vitreous layer. Moreover, silanes having fluorine containing side chains may be used for the formation of the layers provided according to the present invention, resulting in a surface of low energy.

Specifically the present invention provides a process for providing a metallic surface with a vitreous layer, which process is characterized in that a coating composition obtainable by a process comprising the hydrolysis and polycondensation of one or more silanes of the general formula (I)



wherein the groups X, the same or different from each other, are hydrolyzable groups or hydroxyl groups, the radicals R, the same or different from each other, represent hydrogen, alkyl, alkenyl and alkynyl groups having up to 12 carbon atoms and aryl, aralkyl and alkaryl groups having 6 to 10 carbon atoms and n is 0, 1 or 2, provided that at least one silane having  $n=1$  or 2 is used, or oligomers derived therefrom, in the presence of

- a) nanoscaled  $SiO_2$  particles and/or
- b) at least one compound selected from the group consisting of the oxides and hydroxides of alkali and alkaline earth metals,

is applied onto said metallic surface and the resulting coating is thermally densified to form a vitreous layer, optionally (and preferably) preceded by a drying operation.

In the present context the above mentioned "nanoscaled  $SiO_2$  particles" are to denote  $SiO_2$  particles having an average particle size (or an average particle diameter) of not more than 200 nm, preferably of not more than 100 nm and particularly preferred of not more than 50 nm, an upper limit of 30 nm being particularly preferred.

The process according to the present invention will in the following be explained in more detail.

Among the above silanes of the general formula (I) there is at least one silane in the formula of which  $n$  has the value of 1 or 2. Usually at least two silanes of the general formula (I) are employed in combination. In that case said silanes are employed in such proportions that the ratio  $R:Si$ , i.e., the average value of  $n$  (based on moles) ranges from 0.2 to 1.5, preferably from 0.5 to 1.0. It is particularly preferred for said average value of  $n$  to range from 0.6 to 0.8.

In general formula (I) the groups  $X$ , which may be the same or different from each other, represent hydrolyzable groups or hydroxyl groups. Specific examples of hydrolyzable groups  $X$  are halogen atoms (particularly chlorine and bromine), alkoxy groups and acyloxy groups having up to 6 carbon atoms. Particularly preferred are alkoxy groups, especially C1-4 alkoxy groups such as methoxy, ethoxy and *n*- and *i*-propoxy. Preferably the groups  $X$  in a specific silane are identical, methoxy or ethoxy groups being preferably employed.

The groups  $R$  in general formula (I) which for  $n=2$  may be the same or different represent hydrogen, alkyl, alkenyl and alkynyl groups having up to 12 (generally up to 8 and preferably up to 4) carbon atoms and aryl, aralkyl and alkaryl groups having 6 to 10 carbon atoms. Specific examples of such groups are methyl, ethyl, propyl and butyl, vinyl, allyl and propargyl, phenyl, tolyl, benzyl and naphthyl. Usually the groups  $R$  are unsubstituted. As already mentioned above it may, however, be advantageous to employ at least in part groups  $R$  which contain fluorine atoms, particularly alkyl groups and aryl groups having fluorine atoms (preferably not on C-atoms in  $\alpha$ - or  $\beta$ -position with respect to Si, however). The corresponding alkyl groups preferably contain more than 3 carbon atoms and with the exception of the  $\alpha$ - and  $\beta$ -C-atoms they are preferably perfluorinated.

Preferred groups  $R$  are (unsubstituted) alkyl groups having 1 to 4 carbon atoms, especially methyl and ethyl, as well as phenyl; and additionally fluorinated alkyl groups having 4 to 12 carbon atoms.

According to the present invention it is preferred to employ at least two silanes of the general formula (I), wherein in at least one case  $n=0$  and in the other case  $n=1$ . Such mixtures of silanes comprise, for example, at least one alkyltrialkoxy silane (e.g. (m)ethyltri(m)ethoxy silane) and at least one tetraalkoxy silane (e.g. tetra(m)ethoxy silane), which silanes are preferably employed in such proportions that the average value of  $n$  is in the preferred range specified above.

The nanoscaled  $SiO_2$  particles which are employed according to variant (a) of the process according to the present invention in addition to the hydrolyzable silanes of the general formula (I) are preferably employed in such an amount that the ratio of the total Si-atoms in the silanes of the general formula (I) to the total Si-atoms in the nanoscaled  $SiO_2$  particles ranges from 5:1 to 1:2, particularly from 4:1 to 2:1. Such nanoscaled  $SiO_2$  particles may for example be employed in the form of commercially available silica sols (obtainable e.g. from the company Bayer).

As an alternative or in addition (preferably as an alternative) to the presence of said nanoscaled  $SiO_2$  particles the hydrolysis and polycondensation of the silane(s) of the general formula (I) may be carried out in the presence of at least one compound from the group of the oxides and hydroxides of alkali and alkaline earth metals. Said oxides and hydroxides are preferably those of Li, Na, K, Mg, Ca and/or Ba. The use of alkali metal hydroxides, especially NaOH and KOH, is particularly preferred. When using an alkali metal oxide or hydroxide, respectively, it is preferred to employ same in such an amount that the atomic ratio Si:alkali metal ranges from 20:1 to 5:1, especially from 15:1 to 10:1. In any event, the atomic ratio of silica to alkali and/or alkaline earth metal is selected (high enough) so that the resulting coating is substantially insoluble in water.

It is believed that also in the case of variant (b) of the process according to the present invention nanoscaled  $SiO_2$  particles are present (which are employed as such in the case of variant (a)),

i.e., are formed in situ so that there is no fundamental difference between said variants (a) and (b). Rather, it is assumed that the presence of nanoscaled SiO<sub>2</sub> particles in the coating is of essential importance for achieving sufficient layer thicknesses. It is also believed that the presence of groups R in the starting silanes i.a. serves to prevent too strong a crosslinking of the organic SiO<sub>2</sub> skeleton (and thereby too strong a stiffening and embrittlement, respectively, of the layer).

The difference between the above variants (a) and (b) resides--if at all--in that in the case of variant (a) the hydrolysis and polycondensation of the silanes of the general formula (I) is usually acid-catalyzed, (preferably inorganic) acids such as hydrochloric acid, nitric acid and (preferably) phosphoric acid being used as catalysts. In contrast thereto, in the case of variant (b) hydrolysis and polycondensation apparently take place in an alkaline medium, which is advantageous especially in the case where metallic surfaces which are not or only slightly resistant to the attack by acids (e.g. made of steel) are to be provided with a vitreous coating according to the process of the present invention. A further advantage of variant (b) is that due to the content of alkaline earth or alkali metals the densification is improved so that, for example, the coating operation can take place in an atmosphere of air without causing damage (blushing) of the underlying metallic (e.g. steel) surface. By using variant (b) it is further possible to provide steel for construction (e.g. ST37, ST50) with a vitreous layer, if carried out with exclusion of air (N<sub>2</sub> atmosphere), without causing blushing of the steel upon densification.

The coating composition applied on the metallic surface will subsequently be thermally densified to form a vitreous layer. Prior to said thermal densification a conventional drying operation of the coating composition at room temperature and/or slightly elevated temperature (e.g. at a temperature of up to 100 DEG C., particularly up to 80 DEG C.) will usually be carried out.

Although the (final) temperature of the thermal densification must also be determined in consideration of the heat resistance of the metallic surface, said temperature is usually at least 300 DEG C., particularly at least 400 DEG C. and particularly preferred at least 500 DEG C. If the metallic surface is sensitive to oxidation, especially at such high temperatures, it is recommended to carry out said thermal densification in a oxygen-free atmosphere, e.g. under nitrogen or argon.

According to the present invention, the thickness of the vitreous layer obtained after the thermal densification preferably ranges from 1 to 10 .mu.m, particularly 2 to 7 .mu.m and particularly preferred 3 to 5 .mu.m.

As already mentioned above, (at least) one further (vitreous) layer may be provided on the (usually transparent and colorless) vitreous layer formed according to the process of the present invention, e.g., a functional vitreous layer as it is described in international patent application PCT/EP94/03423 (corresponding to EP-A-729442), or in DE-A-19645043.

Such further layers will, for example, be applied by mixing a composition which is obtainable by hydrolysis and polycondensation of certain (functionalized) silanes with at least one function carrier from the group of the temperature resistant dyes and pigments, metal or non-metal oxides, coloring metal ions, metal or metal compound colloids and metal ions which form metal colloids under reducing conditions, applying the composition mixed with said function carrier onto the surface to be coated and thermally densifying the coating to form a (colored) vitreous layer. Alternatively, a (colored) layer may be provided by applying onto the surface to be coated a coating composition containing at least one element capable of forming a vitreous, crystalline or partially crystalline oxide in the form of a compound which is capable of affording said oxide upon thermal treatment and is present in an at least predominantly aqueous medium as solution or sol, as matrix-forming component, and at least one member from the group of metal, metal compound and metal alloy colloids and metal compounds forming metal colloids under reducing conditions, as coloring component, and thermally curing the resulting coating. As elements capable of forming a vitreous, crystalline or partially crystalline oxide Ti and Zr may, for example, be mentioned.

Such a colored vitreous layer may be provided on the vitreous layer produced according to the present invention, for example by providing the coating which is formed according to the present invention on the metallic surface prior to the thermal densification (and preferably following its drying at room temperature and/or elevated temperature) of the former with a coating composition for said colored vitreous layer and thermally densifying said two coatings together. It is, of course, also possible to incorporate coloring components (for example the ones mentioned above) directly into the coating composition to be employed according to the present invention, but this is not preferred.

As metallic surfaces to be coated according to the present invention all surfaces consisting of (or comprising, respectively) a metal or a metal alloy are suitable.

As examples for metal alloys (stainless) steel, brass or bronze are to be mentioned particularly, the coating of stainless steel being particularly preferred according to the present invention.

As examples of metallic surfaces those of aluminum, tin, zinc, chromium or nickel (including zinc- or chromium-plated surfaces) may be mentioned.

Prior to the application of the coating composition the metallic surface is preferably thoroughly cleaned (particularly freed of grease and dust). Prior to the coating operation a surface treatment (e.g. by roughening or corona discharge) may be carried out but is neither necessary nor preferred according to the present invention.

The hydrolysis and polycondensation of the silanes of the general formula (I) may be carried out in the presence or absence of an organic solvent. Preferably no organic solvent is present. When using an organic solvent, the starting components are preferably soluble in the reaction medium (which usually includes water). As organic solvents water-miscible solvents such as, e.g., mono- or polyhydric aliphatic alcohols (e.g. methanol, ethanol), ethers (such as diethylether), esters (such as ethylacetate), ketones, amides, sulfoxides and sulfones are particularly suitable. Said solvents may optionally also be added to the final coating composition in order to provide a viscosity which is suitable for the coating operation.

Otherwise, hydrolysis and polycondensation may be carried out according to modalities known to the skilled person.

The coating composition employed according to the present invention may be applied onto the metallic surface according to conventional coating methods. Examples of techniques which may be employed are dipping, casting, spinning, spraying or brushing. Particularly preferred are dipping processes.

It remains to be noted that the thermal densification may optionally also be effected by IR or laser radiation. Also, it is possible to produce structured coatings by selective action of heat thereon.

The process according to the present invention is particularly--but not exclusively--suited for the coating of articles of everyday use which have a metallic surface or consist of metal, respectively. Thus, metallic surfaces (e.g. steel surfaces) which can be found, e.g., with panels, cuttlery, bowls, sinks, door and window handles and the like may be coated.

The present invention provides a decorative system which can advantageously be applied onto metallic surfaces (e.g. made of (stainless) steel), is weathering resistant and insensitive to scratching and also assists in the prevention of staining, e.g., by fingerprints, etc.

The following examples illustrate the present invention.

#### EXAMPLE 1

#### Preparation of a SiO<sub>2</sub> coating sol

A mixture of 20 ml of methyltriethoxy silane and 6 ml of tetraethoxy silane is provided and with vigorous stirring 15 g of silica sol (Bayer Kieselcol Typ 300, 30% by weight (concentrated to 45% by weight)) is added thereto. Following the formation of an emulsion (after about 20 seconds) 0.3 ml of H<sub>3</sub> PO<sub>4</sub> (concentrated) are added to initiate the hydrolysis. The mixture stays turbid for another 20 to 60 seconds and thereafter immediately turns first viscous and then highly liquid and clear. During said reaction the temperature of the sol increases to about 40 DEG C. Following the cooling to room temperature (optionally in an ice bath) the resulting sol is filtered through a filter of a pore size of 0.8  $\mu\text{m}$  (having a prefilter of a pore size of 5  $\mu\text{m}$ ). The viscosity of the sol thus prepared may be adjusted to a desired value by means of e.g. ethanol, propanol or alcohol mixtures and it may be used for the coating operation for at least 6 hours.

#### EXAMPLE 2

##### Preparation of a sodium silicate coating sol

25 ml (124.8 mmoles) of methyltriethoxy silane (MTEOS) are stirred with 7 ml (31.4 mmoles) of tetraethoxy silane (TEOS) and 0.8 g (20 mmoles) of sodium hydroxide overnight (for at least 12 hours) at room temperature until all of the sodium hydroxide has dissolved and a clear yellow solution is formed.

Subsequently 3.2 ml (177.8 mmoles) of water are slowly added dropwise at room temperature, resulting in a rise of the temperature of the solution. After completion of the addition of water the clear yellow solution is stirred at room temperature until it is cooled off again and is subsequently filtered through a filter having a pore size of 0.8  $\mu\text{m}$ .

#### EXAMPLE 3

##### Preparation of a potassium silicate coating sol

Example 2 is repeated, except that 0.8 g of sodium hydroxide is replaced by 0.8 g (12.1 mmoles) of potassium hydroxide.

#### EXAMPLE 4

Cleaned substrates (stainless steel 1.4301, brass and aluminum) were dip-coated at a drawing speed of 4-6 mm/s with the coating compositions described in Examples 1 to 3, predried for a short period of time (10 minutes) at room temperature and subsequently dried at 80 DEG C. for 1 hour. For densification the dried substrates were heated in air (or under nitrogen in the case of coating stainless steel with the coating composition from Example 1) at a heating rate of 1 K/minute to 500 DEG C. (or 400 DEG C. in the case of aluminum) and maintained at said temperature for 1 hour.

The layer thicknesses after the densification were 2 to 4  $\mu\text{m}$ . HREM studies on the coatings on steel and aluminum showed a layer free of defects.

The blushing of the stainless steel upon densification could almost completely be prevented by the coating. Furthermore the layer showed no damaged portions even after 1000 hours in the salt spray test.

The coated brass and aluminum showed no corrosion damage after 3000 hours of corrosion test in the salt spray chamber (DIN 50021), whereas the part that had not been coated became completely corroded.

## EXAMPLE 5

Standard anti-adhesion material MTKF 1% by mole of FTS

Methyltriethoxy silane (MTEOS) (0.2 moles, 35.7 g) and TEOS (0.054 moles, 11.3 g) are stirred in a suitable vessel (e.g. a 250 ml Schott bottle) and 0.1 moles of SiO<sub>2</sub> (in 20.0 g of silica sol 300/30%) are added thereto. After 5 minutes 0.4 g of concentrated HCl are added with intensive stirring. The initial two-phase reaction mixture turns white after 2 minutes, heats up and becomes transparent and single-phased again. After 15 minutes of reaction 3.0 g of DOWEX.RTM.50W2 are added and the resulting mixture is stirred for 10 minutes. Subsequently, a pressure filtration through a fiberglass prefilter is carried out. Immediately thereafter 1.78 g (1% by mole based on Si) of 1H,1H,2H,2H-perfluorooctyltriethoxy silane (FTS) are added and the sol is stirred again for 15 minutes. Amberlyst.RTM.A-21 (4.0 g) is added and stirring is continued for 30 Minutes. Following a pressure filtration through a membrane filter (pore size 1 .mu.m) 140 g of isopropanol are added for dilution. Following a pressure filtration through a membrane filter (pore size 0.2 .mu.m) the sol is finally ready for the coating operation.

The application of the sol onto a stainless steel surface is carried out by means of spraying and the curing is effected at 350 DEG C. under an air atmosphere. The material of the coating is a transparent anti-adhesion layer showing contact angles of 110 DEG against water and of 60 DEG against hexadecane, respectively.

## EXAMPLE 6

Alkalinely hydrolyzed system having 11% by moles of FTS

A suitable Schott bottle is charged with 0.1 moles (17.9 g) of MTEOS, 0.027 moles (5.6 g) of TEOS and 0.016 moles (8.16 g; 11% by mole based on Si) of FTS. Subsequently, 0.018 moles of NaOH (0.72 g) are added with stirring and stirring is continued for about 16 hours. Thereafter, 0.15 moles (2.7 g) of H<sub>2</sub>O are added dropwise to the solution which meanwhile has turned yellow. After completion of the addition stirring is continued for about 30 minutes. Subsequently the mixture is diluted with 35 g of ethanol and filtered through a 1 .mu.m filter by means of pressure filtration.

The final sol is applied on a stainless steel plate by means of spray coating and cured at 350 DEG C. under an atmosphere of air. Said system does not show the discoloration of substrates made of stainless steel which is usually observed at these temperatures. The layer is completely transparent and shows contact angles against water of 95 DEG and against hexadecane of 40 DEG, respectively.

We claim:

1. A process for providing a metallic surface with a vitreous layer, comprising:  
(a) preparing a coating composition by a process comprising hydrolyzing and polycondensing one or more silanes of the formula

$R_n SiX_{4-n}$ ,

where

each R, which may be the same or different, is hydrogen, or an optionally fluorinated alkyl, alkenyl, or alkynyl group having up to 12 carbon atoms, or an optionally fluorinated aryl, aralkyl, or alkaryl group having 6 to 10 carbon atoms,

each X, which may be the same or different, is a hydrolyzable group or a hydroxyl group, and n is 0, 1 or 2, provided that at least one silane has n=1 or 2, or one or more oligomers derived therefrom,

in the presence of nanoscale SiO<sub>2</sub> particles and at least one compound selected from the group



consisting of the oxides and hydroxides of the alkali and alkaline earth metals, where the ratio of total Si atoms in the one or more silanes to total alkali metal and alkaline earth metal atoms in the at least one compound selected from the group consisting of the oxides and hydroxides of the alkali and alkaline earth metals is between 20:1 and 5:1;  
(b) applying the coating composition to the metallic surface to form a coating; and  
(c) thermally densifying the coating to form a transparent vitreous layer.

2. A process of claim 1 where the average value of n is between 0.2 and 1.5.
3. A process of claim 1 where the or each X is alkoxy.
4. A process of claim 3 where the or each X is methoxy or ethoxy.
5. A process of claim where the or each R is optionally fluorinated C1-4 alkyl or phenyl.
6. A process of claim 1 where the one or more silanes are one or more of methyltrimethoxysilane, methyltriethoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, tetramethoxysilane, and tetraethoxysilane.
7. A process of claim 1 where at least one R of the one or more silanes is fluorinated.
8. A process of claim 1 where the ratio of total Si atoms in the one or more silanes to total Si atoms in the nanoscale SiO<sub>2</sub> particles is between 5:1 and 1:2.
9. A process of claim 1 where the at least one compound selected from the group consisting of the oxides and hydroxides of the alkali and alkaline earth metals comprises one or more of the oxides and hydroxides of Li, Na, K, Mg, Ca, and Ba.
10. A process of claim 9 where the at least one compound is sodium hydroxide or potassium hydroxide.
11. A process of claim 1, additionally comprising drying the coating before thermally densifying it.
12. A process of claim 1 where thermally densifying the coating takes place at temperatures of at least 400 DEG C.
13. A process of claim 1 where the thickness of the resulting layer is between 1 .mu.m and 10 .mu.m.
14. A process of claim 1 for providing a metallic surface with a colored vitreous layer, additionally comprising:  
applying to the metallic surface having a coating thereon at least one further coating composition, which upon thermal densification results in a colored vitreous layer, to form a further coating; and  
thermally densifying the further coating to obtain a colored vitreous layer.
15. A process of claim 1 for providing a metallic surface with a colored vitreous layer, additionally comprising:  
applying to the metallic surface having a transparent vitreous layer thereon at least one further coating composition, which upon thermal densification results in a colored vitreous layer, to form a further coating; and  
thermally densifying the further coating to obtain a colored vitreous layer.
16. A process of claim 1 where the metallic surface is a metal alloy.
17. A process of claim 1 where the metallic surface is aluminum, tin, zinc, chromium, or nickel.

18. A process of claim 1 where the metallic surface is the metallic surface of a panel, item of cutlery, cooking utensil, sink, or a door or window handle.

## Refractory Coatings

## Refractory Coatings

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LAM PARTNERSHIP

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☐ NL7904208, SE7904633, ZA7902663

### Abstract

A method for "hot end" coating of vitreous articles, comprises forming refractory magnesium oxide coatings from aqueous solutions of magnesium nitrate, acetate or formate which are applied to the vitreous surface at an elevated temperature to evaporate the water from the solution and pyrolytically decompose magnesium compound to form a transparent magnesium oxide coating. A

lubricious coating comprising at least one of waxy polyolefins, beeswax, fatty acids or alkali metal salts thereof, or polyvinyl alcohol may be applied to the coating.

#### SPECIFICATION

##### Process for Coating Vitreous Article, and Such Coated Articles

The present invention relates generally to refractory "hot end" coatings for vitreous articles such as glassware, and more particularly to improved methods for forming magnesium oxide "hot end" coatings upon glassware from aqueous solutions, and to articles so coated.

The desirability of forming refractory coatings on vitreous surfaces, such as glass, and particularly upon glassware such as bottles, is well known. Pristine glass is theoretically and extremely strong substance. However, when, for example, glassware is subjected to high speed processing machines and normal use in which glass is caused to rub against glass, scratches, abrasions, and other physical damage rapidly degrades the surface of the glass thereby providing sites for initiation of failure throughout the glass. Also, glass is subject to attack by various atmospheric constituents, particularly moisture. Accordingly, it has been an accepted practice in the production of glassware to form a refractory, so-called "hot-end" coating upon the newly formed glass, usually at or before the annealing lehr while the glassware is at an elevated temperature. After formation of a refractory "hot end" coating, it is conventional practice to thereafter apply a lubricious "cold end" coating at lower temperatures. "Cold end" coatings conventionally include, for instance, waxy polyethylene, fatty acids, beeswax, and other such lubricious compositions, either alone or in combination.

The "hot end" coatings, to which the present invention pertains, display particular requirements which distinguish "hot end" coatings from a number of other coatings previously employed upon glass for various purposes. For instance, thick coatings of tin oxide and magnesia have been applied to, for instance, electrical insulators.

Other thick coatings of tin oxide have been applied to provide electrical conductivity for defrosting of glass surfaces by employing the tin oxide coating as a resistance element. Semitransparent, colored coatings have been utilized for decorative purposes and, in some instances, for tinting of glass.

"Hot end" coatings have a number of requirements not met by many known glass coatings. Typically, such coatings should be nontoxic as a coating, and also are desirably formed from compositions which are not in themselves toxic and which do not form toxic byproducts. The coatings formed should not change the appearance of the glassware, i.e., are colorless and substantially free of iridescence. Torque requirements of closures should not be altered.

Since glassware is formed at high rates, coatings must be conveniently applied and utilize relatively economical solvents and compounds. Further, "hot end" coatings must be resistant to normal handling and processing, such as washing, and must tenaciously adhere to the glass to provide a suitable base for lubricious "cold end" coating.

Contrary to the purpose of certain other glass coatings, "hot end" coatings should have high electrical resistance to avoid galvanic action between, for instance, container closures and other materials which come in contact with the glass under damp conditions. The "hot end"

coating itself should not function as an electrolyte in contact with metal closures. Thus, it will be recognized that "hot end" coatings or glassware are a well recognized group of materials having characteristics and requirements distinct from other glass coatings.

Currently, "hot end" coatings are generally tin oxide or titanium oxide, formed from vapors of anhydrous tin or titanium tetrachloride or from aqueous solutions of such compounds. However, previously "hot end" coatings of tin, titanium or zirconium oxide have also been formed from organic compounds applied in or from organic solutions.

A number of prior art discussions exist concerning the various coatings. For instance, U.S. Letters Patent 2,165,819, issued July 11, 1939, discloses an electrical insulator of magnesium titanate suitable for formation on ceramic substances such as condensers.

Magnesium titanate is disclosed as being suitable for a narrow, and quite specific coating purpose, but does not correlate with the requirements of a "hot end" coating.

U.S. Letters Patent 3,323,889, issued June 6, 1967, discloses a coating system for the purposes of the instant invention, but involves the use of zirconium and titanium oxide as a "hot end" coating applied from an organic solvent solution in conjunction with relatively conventional "cold end" coatings. Many organic solvents are expensive, often flammable, and cause objectionable pollution of the atmosphere.

However, U.S. Letters Patent 3,323,889 is pertinent in setting forth many of the requirements of a "hot end" coating.

U.S. Letters Patent 3,450,574, issued June 17, 1969, is concerned with the preparation of a magnesia coating on refractory bodies. Preferably, the patent teaches the formation of a thin film of metal under reducing conditions and thereafter providing oxidizing conditions to form the oxide.

Sintering techniques are also disclosed.

U.S. Letters Patent 3,516,811, issued June 23, 1970, primarily discloses apparatus for applying "hot end" coatings in laminar flow condition, but also contains a fairly comprehensive listing of various prior art patents dealing with "hot end" and "cold end" coatings.

Typical of the hot end coatings discussed by U.S. Letters Patent 3,516,811 is U.S. Letters Patent 3,561,940, issued February 9, 1971, which concerns the formation of tin oxide coatings by the pyrolytic composition of anhydrous stannic tetrachloride vapors in a moisture-free carrier gas. While tin oxide is a desirable and workable "hot end" coating, the by products of the pyrolytic decomposition include hydrochloric acid (upon hydrolysis with atmospheric moisture) which presents serious problems with regard to attack of surrounding equipment and pollution of the atmosphere. Such installations may require expensive scrubbing equipment to remove the unused stannic tetrachloric and hydrochloric acid from the exhaust gases.

U.S. Letters Patent 3,694,299, issued September 1972, discloses a means for fusing glass sheets together utilizing an organometallic film forming solution in which the metallic constituent may include magnesium.

However, the solution utilizes volatile and combustible solvents as well as resins which would be

entirely inappropriate for use in a "hot end" coating composition for the reasons discussed above.

U.S. Letters Patent 3,711,322, issued January 16, 1973, discloses organic solvent based compositions utilizing two metal compounds, one of which may be a magnesium compound such as magnesium acetate, to form semi-transparent, colored metal oxide coatings. For numerous reasons including transparency, color, organic solvents, etc., such coatings would not be useful as "hot end" coatings.

U.S. Letters Patent 3,847,583, issued November 12, 1974, similarly discloses the use of two metal compounds dissolved in an organic solvent to form coatings. Titanium oxide and, it is believed, tin oxide, are discussed, and specific mention is made that alkali or alkali earth oxides are not operable to form pyrolytically induced oxide coatings.

U.S. Letters Patent 3,926,103, issued December 16, 1975, discloses a recovery system for a spray solutions of tin compounds.

Finally, U.S. Letters Patent 3,984,591, issued October 5, 1976, discloses the formation of metallic oxide coatings from metallic salts utilizing, as a critical feature of the invention, aprotic solvents of specific dipolar moments which would be inappropriate for "hot end" coatings. Mention is made of spraying aqueous solutions, but such coatings are characterized as being readily removed in the form of dust by passing a finger over the coating.

Thus, on the basis of the above prior art, the only workable "hot end" coatings are those involving pyrolytic decomposition from objectionable organic solvents or from halides. In both cases, objectionable by-products in the form of exhaust fumes are presented. The better, more economical coatings involve pyrolytic decomposition of stannic tetrachloride with the resulting formation of hydrochloric acid.

The present invention, which provides a heretofore unrecognized and unavailable improvement over previous methods for forming "hot end" coatings on glassware, involves pyrolytic decomposition of solutions of water soluble magnesium compounds which, directly or indirectly, form magnesium oxide containing coating upon glassware heated above about 450°C, preferably between 500--700°C.

Particularly, magnesium acetate, which provides high quality coatings with innocuous by-

products, and also magnesium nitrate which forms a desirable coating with less desirable by-products are preferred, though other magnesium compounds have also been found to be operable if sufficiently water soluble.

Accordingly, advantage of the present invention is to provide a new and improved coating method and refractory coating for glassware which adheres strongly to the glassware and does not substantially alter the appearance of the glassware.

Another advantage of the present invention is to provide a new and improved coating method and coating for glassware which displays an affinity for "cold end" coatings and provides both wet and dry lubrication with such "cold end" coatings.

Still another advantage of the present invention is to provide a new and improved coating method and improved coating for glassware which coating is non-toxic.

These and other advantages of the present invention will be apparent from the following description of the invention.

According to the present invention, "hot end" coatings of magnesium oxide are formed on vitreous substances such as glassware by applying an aqueous solution of magnesium compounds having specific properties to glassware heated to an elevated temperature, i.e., above 400°C to 4500°C, and preferably above about 5500°C. Typically, such surfaces are not heated above 7000°C, but in specific instances may be heated to higher temperatures without adversely affecting the coating in accord with the instant invention. The limiting upper temperature depends upon the substrate and the coating and the lower temperature depends upon the coating.

Many of the advantages of the instant invention accrue from the use of aqueous solutions of the magnesium compounds. Essentially, the compounds must be water soluble magnesium compounds. The magnesium compounds are dissolved in a water carrier and are sprayed upon the hot glassware preferably in the form of a mist or fine spray of the solution. It is also important that the magnesium compound decompose to magnesium oxide at the temperatures existing on the surface of the glassware and, preferably, after initially melting as the dissolved magnesium compound.

While the mechanism is not entirely understood, it is postulated that the magnesium compound is deposited as a solid upon the heated glassware as the solvent is evaporated from the solution. The magnesium compounds initially melt and then pyrolytically decompose to form magnesium oxide. Accordingly, if the original magnesium compound, or any magnesium compound other than magnesium oxide formed during the course of pyrolytic decomposition is stable at the temperature involved, satisfactory results will not be obtained. For instance, most magnesium compounds which are water soluble and include sulfur, i.e. magnesium sulfate heptahydrate  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , and other such magnesium compounds including sulfur, i.e., magnesium thiosulfate  $\text{MgS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ , magnesium sulphite  $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$  which form, upon initial decomposition, magnesium sulfate  $\text{MgSO}_4$  (decomposition temperature of about 1240°C) are not workable. This temperature is above that to which glassware can conventionally be heated. Thus the final coating is magnesium sulfate rather than magnesium oxide and does not display desirable "hot end" coating characteristics. However, such sulfur containing compounds would be expected to provide good results in some instances at higher temperatures with, for instance, ceramics.

Examples of magnesium compounds which meet the above criteria and form worthwhile "hot end" coatings include magnesium acetate, magnesium nitrate, and magnesium formate. As mentioned earlier, the sulfur containing compounds generally are not decomposable to

magnesium oxide under the available temperatures.

Other magnesium compounds such as magnesium benzoate  $\text{Mg}(\text{C}_7\text{H}_5\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ , magnesium lactate  $\text{Mg}(\text{C}_6\text{H}_5\text{O}_7) \cdot 3\text{H}_2\text{O}$ , magnesium citrate  $\text{MgHC}_6\text{HO}_7 \cdot 5\text{H}_2\text{O}$  and magnesium dicitrate  $\text{Mg}_2(\text{C}_6\text{H}_5\text{O}_7) \cdot 5\text{H}_2\text{O}$  appear to be too insoluble to provide clear, adherent coatings. While coatings are formed, the coatings tend to be cloudy and water soluble. This appears to be a function of the solubility of the magnesium compound. Highly soluble magnesium compounds, as discussed above, are believed to form small particles of the compound upon the glassware which particles are believed to immediately melt into a smooth continuous layer of the compound, and then pyrolytically decompose into magnesium oxide. Water insoluble or marginally soluble magnesium compounds do not yield the desired results, possibly because of the formation of solid magnesium compound particles in the presence of substantial quantities of solvent which do not melt into a smooth layer prior to pyrolytic decomposition.

Of the magnesium compounds which satisfy the basic criteria, i.e., high water solubility, melting point below the general surface temperature of heated glass, and pyrolytic decomposition into magnesium oxide at the surface temperature of the glass, magnesium acetate is a particularly preferred composition having properties significantly superior to those of other of the operable magnesium compounds. For instance, magnesium acetate is highly soluble in water, generally employed at between 10 parts by weight of water to one part by weight of magnesium acetate to one part by weight of water to one part by weight of magnesium acetate, and typically at five parts by weight of water to one part by weight of magnesium acetate, and melts at  $800^\circ\text{C}$  and decomposes at  $3230^\circ\text{C}$ , presumably into magnesium oxide. Upon decomposition, magnesium acetate forms water and carbon dioxide as by-products. Magnesium oxide, magnesium acetate and the byproducts are all non-toxic and non-corrosive materials.

Operably magnesium oxide formed by applying magnesium acetate in an aqueous solution to reheated glassware may be produced at surface temperatures above about  $4000^\circ\text{C}$  to  $4500^\circ\text{C}$ .

However, the preferred range is between  $6800^\circ\text{C}$  to  $7000^\circ\text{C}$ . Below about  $5500^\circ\text{C}$  to  $6000^\circ\text{C}$ , the transparency of the coating become somewhat uneven. Above about  $6800^\circ\text{C}$  to  $7000^\circ\text{C}$ , the "hot end" coating lubrication qualities diminish somewhat, particularly when wet. With newly formed glassware with internal temperatures higher than the surface temperature, lower initial temperature may be operable.

Magnesium nitrate forms excellent coatings from aqueous solutions, but forms  $\text{NO}_x$  by products upon pyrolytic decomposition. However, magnesium nitrate melts at  $890^\circ\text{C}$  and decomposes at  $3300^\circ\text{C}$  yielding excellent coatings at normal "hot end" glass coating temperatures.

The resulting magnesium oxide "hot end" coatings in accord with the instant invention should, of course, be thick enough to afford substantial protection to the protected vitreous surface, such

as glassware. However, in most instances, the coating should not be thicker than about one wavelength of light to which it is typically exposed, i.e., about one micron, to avoid wave interference within the coating leading to iridescence. In some instances, coatings may be thicker without otherwise degrading the results.

Iridescence, at times, is considered a desirable appearance. Also, thicker coatings tend to be more electrically conductive. As a rule, the coating thickness may be easily controlled by regulating the exposure time of the heated glassware to a given concentration of the magnesium compound aqueous solution.

As discussed above the magnesium compound should be applied to a reheated surface at at least about 4000C, preferably between 5500C and 7000 C, though higher temperatures are suitable for coating purposes. In most instances though, the vitreous surface may be adversely affected by higher temperatures, though certain vitreous surfaces, such as ceramic, may be heated to quite elevated temperatures. Somewhat lower temperatures may be employed with newly formed glass. Each magnesium compound suitable for forming magnesium oxide coatings in accord with the instant invention of course -display differing melting points and pyrolytic decomposition points. Accordingly, optimum temperatures may vary somewhat from compound to compound, though the above specified temperatures are generally operable. For instance, magnesium acetate is preferably applied to reheated surfaces between 6800C and 7000 C, though good results may be obtained outside of this range.

The concentration of the magnesium compound in aqueous solution is not critical. Of course, more dilute solutions require evaporation of greater quantities of water and accordingly cool the glassware surface more. As a rule, between about 10% to 50% by weight of magnesium compound to weight of solution has been found to be a desirable operating range, though not a critical range. Preferably about midpoint of this range is employed.

It should be noted that the solubility of the magnesium compound in water is an independent consideration from that of the actual concentration of the magnesium compounds in solution when applied to vitreous surfaces. Thus, compounds which marginally dissolve at the above-specified concentration are not necessarily desirable coating compounds. As the water evaporates, solid particles of the magnesium compound is of course formed on the vitreous surface. This result can be prematurely accomplished in near saturated solutions of magnesium compounds. Accordingly, while not firmly established, it is believed that the more highly soluble magnesium compounds operable in the instant invention do not form solid particles until but small amounts of water remain thereby minimizing the concurrent existence of solid matter and solution and leading to melting of the particles to form an initial coating.

It is contemplated that the magnesium oxide coatings formed in accordance with the instant invention will be further coated with lubricious "cold end" coatings as are well known in the art.

Generally, this is accomplished by spraying the lubricious coatings, usually as aqueous solutions, onto the vitreous surfaces after, in the case of glassware, annealing is substantially complete.



Vapors of organic lubricious materials may also be employed to accomplish the coating. "Cold end" coatings are well known in the art. Typically such coatings include one or more lubricious constituents such as waxy polyolefins such as polyethylene having a molecular weight between 1000 and 2000, fatty acids such as oleic, palmitic, stearic, lauric, or mixtures thereof, alkali metal salts of fatty acids, beeswax and polyvinyl alcohol. Such "cold end" coatings are well known in the art and are applicable to the magnesium oxide coatings in accord with the instant invention.

A more detailed appreciation of the invention will be gained from the following examples.

#### Example 1

An aqueous solution of magnesium acetate tetrahydrate was prepared by adding one part by weight of the magnesium acetate compound to five parts by weight of water. A glassware article (bottle) was heated to provide a surface temperature of about 64000. The solution of magnesium acetate was sprayed at a flow rate of about .5 grams per second while the glassware was rotated upon a turntable at 78 rpm.

Approximately 16 revolutions of the glassware bottle occurred during an application. A clear, transparent coating of magnesium oxide was formed on the bottle. Thereafter, when the glassware had cooled to 1200 C, a commercial "cold end" coating, i.e. Glas-Lube 1000 available from Crown Chemical Company, diluted by a factor of 100 by weight in distilled water was sprayed at the rate of 1 gram of "cold end" coating solution per second for a period of 5 revolutions of the glassware on the turntable as discussed above. The thus coated article with both "hot end" and "cold end" coatings was tested for lubrication both wet and dry. Under both conditions lubrication was found to be excellent when two such glassware articles were manually rubbed together.

#### Example 2

A glassware article was coated utilizing the same techniques and compositions as in Example 1 with the exception that the article was passed through a coating hood at a rate of about .8 feet per second while the aqueous solution of magnesium acetate was sprayed onto the article through four nozzles arranged to provide uniform coverage of the bottle on one pass through the coated hood. Results substantially identical to those of Example 1 were obtained. Numerous other similar examples of coating of magnesium acetate were carried out with the following observations; excellent coatings were observed utilizing between about 10% by weight (actually 9.1%) of magnesium acetate to water to 50% by weight of magnesium acetate to water; technical grades of magnesium acetate and ordinary tap water were found to be entirely workable; and a preferred range of 5500C to 7000C was established, and a particularly preferred range being 6800C to 7000C was noted, for reheated glass with the lubrication degrading somewhat, particularly when wet at higher temperatures, and the appearance of the coating degraded somewhat at lower temperatures.

#### Example 3

4.1 parts by weight of water and 1 part by weight of magnesium nitrate hexahydrate were mixed to provide a solution of magnesium nitrate.

The thus prepared solution of aqueous magnesium nitrate was applied to a glassware article utilizing substantially identical conditions as those employed in Example 1. The resulting "hot end" coating was transparent and attractive in appearance, and the article after "cold end"

coating provided good lubrication both dry and wet when tested in a manner identical to that utilized in Example 1.

Other tests with magnesium nitrate were conducted with coating results substantially equal to those obtained with magnesium acetate, though lubrication qualities were poorer utilizing more dilute solutions, and were marginal at about 10% by weight and below of magnesium nitrate to water solutions.

#### Example 4

4.4 parts by weight of water and 1 part by weight of magnesium formate were mixed to form an aqueous solution of magnesium formate.

The thus formed aqueous solution of magnesium formate was applied to a glassware article heated to a temperature of about 66000 to 68000 as described in Example 1. An attractive transparent coating was formed. "Cold end" coating was applied as described in Example 1 and the article tested for lubricity. Lubricity was found to be good when dry and fair wet. In general, magnesium formate was found to be an acceptable and desirable "hot end" coating material.

#### Example 5

Ten parts by weight of water and 1 part by weight of magnesium sulfate were mixed to form a magnesium sulfate aqueous solution. The thus formed aqueous solution of magnesium sulfate was applied to a glassware article heated to about 7200C and the article was otherwise treated and coated as described in Example 1. The "hot end" coating was spotty, the article, including additional "cold end" coating, displayed poor lubricity. It is believed that magnesium sulfate formed the coating. Thus, at the temperatures normally employed with glassware, magnesium sulfate was found to be unsatisfactory as having a decomposition point (about 1 1240C) above that of the working range of most glassware.

#### Example 6

3.3 parts by weight of water was mixed with 1 part by weight of magnesium benzoate. The magnesium benzoate did not entirely dissolve in the water. The magnesium benzoate solution formed, which was more dilute than the initial constituents, was decanted and applied to a glassware article heated to a temperature of about 640°C in the manner described in Example 1. The resulting "hot end" coating was cloudy.

After applying a "cold end" coating as described in Example 1, the article was tested for lubricity.

The results were poor because of poor adhesion of the "hot end" coating. It was found that the "hot end" coating would wash off in water. It is believed that magnesium benzoate is not sufficiently soluble to form a clear, adherent coating as required of the magnesium compound in accord with the instant invention. Similar results were obtained with magnesium lactate, magnesium citrate, and magnesium dicitrate, all of which required decanting utilizing similar amounts of water and magnesium compounds.

From the above description, it will be apparent that the instant invention discloses an advantageous means for providing "hot end" coatings upon glassware. Aqueous coating solutions of magnesium compounds are much easier to utilize and yield less troublesome byproducts than the anhydrous compounds previously employed in many instances. Further, one skilled in the art can, with little effort, identify magnesium compounds suitable for use in the instant invention. Such compounds are highly soluble in water, i.e., form solutions of at least 50% by weight, and preferably much higher, of the magnesium compound in water, display melting point below that of the surface to be coated and pyrolytic decomposition point to magnesium oxide below the temperature of the surface to be coated but above the melting point of the magnesium compounds. Actual testing is easily accomplished by substituting various solutions in a coating hood.

In operation, it is preferred to conduct the vitreous articles, and particularly newly formed glassware, through a coating hood in which the aqueous solution of magnesium compound is applied to the bottle as a fine mist or spray.

Surface temperatures of the glassware and concentration of the aqueous magnesium solution are not critical within broad limits but do generally influence the nature of the "hot end" coating.

Highly dilute solutions, of course, may cause objectionable cooling of the unannealed articles.

Although only several specific examples and embodiments of the present invention have been presented in detail, those skilled in the art will recognize numerous changes and modifications within the scope of the invention. Such changes may be made without departing from the scope of the invention, as defined by the following claims.

#### Claims

1. A vitreous article having protective and lubricious coatings thereon, characterized in that the protective coating is a transparent, refractory coating comprising magnesium oxide adhered directly to the surface of the vitreous article.
2. A coated vitreous article as set forth in Claim 1 characterized in that the lubricious coating includes at least one constituent selected from the group consisting of waxy polyolefins, beeswax, fatty acids, alkali metal salts of fatty acids, and polyvinyl alcohols.
3. A coated vitreous article as set forth in either of Claims 1 and 2 characterized in that the magnesium oxide refractory coating is between .1 micron and 1 micron thick.
4. A method for forming protective, refractory coatings upon vitreous articles characterized in that a vitreous article heated to an elevated temperature is positioned within a coating location, a solution of a magnesium compound is applied upon the surface of the heated vitreous article, the solvent from the magnesium compound solution is evaporated at the surface of the vitreous article, and the magnesium compound is pyrolytically decomposed at the surface of the vitreous article to form a continuous, adherent and substantially transparent, refractory coating comprising magnesium oxide upon the surface of the vitreous article.
5. A method for coating vitreous articles as set forth in Claim 4 characterized in that the solution of magnesium compound is an aqueous solution.
6. A method for coating vitreous articles as set forth in either of Claims 4 or 5 characterized in that the surface of the article is at a temperature above 4000C.
7. A method for coating vitreous articles as set forth in any of Claims 4, 5, and 6, characterized in that the surface of the vitreous article is at a temperature between 4000C and 7000C.
8. A method for coating vitreous articles as set forth in any of Claims 4, 5, 6 and 7 characterized in that the magnesium compound is melted after the solvent is substantially evaporated to form a coating of magnesium compound upon the vitreous article surface, and thereafter is pyrolyzed to form the coating of magnesium oxide.
9. A method for coating vitreous articles as set forth in any of Claims 4, 5, 6, 7 and 8 characterized in that the solution of magnesium compound is spread upon the surface of vitreous article in the form of a mist.
10. A method for coating vitreous articles as set forth in any of Claims 4, 5, 6, 7, 8 and 9 characterized in that the magnesium compound is highly soluble in water, has a melting point below the surface temperature of the vitreous article, and a pyrolytic decomposition point below

the surface temperature of the vitreous article and above the melting point of the magnesium compound.

11. A method for coating vitreous articles as set forth in any of Claims 4, 5, 6, 7, 8, 9 and 10 characterized in that the magnesium compound is selected from the group consisting of magnesium acetate, magnesium nitrate and magnesium formate.

12. A method for coating vitreous articles as set forth in any of Claims 4, 5, 6, 7, 8, 9, 10 and 11 characterized in that the magnesium compound is magnesium acetate.

13. A method for coating vitreous articles as set forth in any of Claims 4, 5, 6, 7, 8, 9, 10, 11, and 12 characterized in that the magnesium acetate is applied as a solution comprising between 10% and 50% by weight of magnesium acetate relative to the solvent.

14. A method for coating vitreous articles as set forth in any of Claims 4, 5, 6, 7, 8, 9, 10, 11, 12 and 13 characterized in which the magnesium refractory coating is between about .1 micron and 1 micron thick.

15. A method for coating vitreous articles as set forth in any of Claims 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 and 14 characterized in that the vitreous article is cooled after formation of the magnesium oxide coating and a second lubricious coating is applied thereto at a lower temperature.

16. A method for coating vitreous articles as set forth in any of Claims 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 and 15 characterized in that a lubricious coating including at least one compound from the group consisting of waxy polyolefins, beeswax, fatty acids, alkali metal salts of fatty acids, and polyvinyl alcohols is applied to the magnesium refractory coating.

## **Lamp having silica protective coating**

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Inventor(s):

HOEGLER LEONARD EDWARD (US); PARHAM THOMAS GENE (US); WHITMAN PAMELA KAY (US)

Applicant(s):

GEN ELECTRIC (US)

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#### Abstract

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An electric lamp, such as an incandescent linear quartz heat lamp, is provided having a vitreous light transmissive envelope having an exterior surface and a light source capable of generating light within said envelope. Disposed on a portion of the exterior surface of the envelope is a diffuse reflective coating, such as a boron nitride coating, for reflecting at least a portion of the light emitted by the source. A protective silica coating encapsulates the reflective coating to protect the reflective coating from things such as abrasion, moisture, and cleaning solvents.

#### BACKGROUND OF THE INVENTION

#### FIELD OF THE INVENTION

The present invention generally relates to electric lamps, and more particularly, to electric lamps having a diffuse reflective coating and a silica coating for protecting the diffuse reflective coating.

#### DESCRIPTION OF RELATED ART

It is known to use coatings on lamps which reflect various portions of the spectrum of light emitted from the lamp. Heat-resistant diffuse reflective coatings containing a refractory metal oxide such as zirconia, alumina, titania, etc., with a glass frit binder or a binder such as a mixture of boric acid and silica, have been used on the ends of arc tubes of high intensity discharge lamps, such as metal halide arc discharge lamps. See, for example, U.S. Patent No. 3,374,377, the disclosure of which is expressly incorporated herein in its entirety. The reflective coatings reflect both visible and infrared radiation to maintain a relatively high temperature at ends of the arc tube and prevent ionized metal halides in the arc tube from condensing on otherwise relatively cool ends of the arc tube.

Heat-resistant diffuse reflective coatings comprising boron nitride have also been used on lamps, such as incandescent linear quartz heat lamps. See, for example, U.S. Patent No. 5,168,193, the disclosure of which is expressly incorporated herein in its entirety. The reflective coating is applied to a portion of the outer surface of the lamp envelope for reflecting both visible and infrared radiation emitted by the filament. Applying the reflective coating on half of the linear surface of the envelope maximizes the radiant energy emitted in the direction of an object to be

heated, while minimizing the radiant energy emitted in the opposite direction.

The diffuse reflective coatings or powder coatings are not very durable and typically have a relatively low abrasion resistance. Therefore, lamps having exposed coatings require careful shipping and handling. The diffuse reflective coatings which are water based, such as the boron nitride coatings, are also easily washed off. This is particularly a problem in industrial settings having the potential for condensation to build up when the lamp is cool. The condensation can build up and gradually wash off the diffuse reflective coating. Additionally, in many industrial settings the lamps are cleaned with acetone which washes off the diffuse reflective coating. Accordingly, there is a need for a protective overcoat for diffuse reflective coatings that increases abrasion resistance, increases moisture and acetone resistance, does not degrade the performance of the lamp, is relatively inexpensive to apply, and will withstand the high temperature conditions and thermal cycling experienced on incandescent and arc discharge lamps.

## SUMMARY OF THE INVENTION

The present invention relates to an electric lamp having a silica protective coating that overcomes the above-described problems of the related art. According to the invention, the lamp includes a vitreous light transmissive envelope having an exterior surface and a light source capable of generating light within the envelope. Disposed on at least a portion of the exterior surface of the envelope is a diffuse reflective coating for reflecting at least a portion of the light emitted by the source. Disposed on the reflective coating is a protective silica coating to protect the reflective coating.

## BRIEF DESCRIPTION OF THE DRAWINGS

These and further features of the present invention will be apparent with reference to the following description and drawings, wherein:

FIG. 1(a) is a side elevational view of an incandescent linear quartz heat lamp having an envelope with a diffuse reflective coating and a silica protective coating according to the present invention;

FIG. 1(b) is an end elevational view of the lamp of FIG. 1(a); and

FIG. 2 is a side elevational view of an arc lamp having an arc tube with a diffuse reflective coating and a silica protective coating according to the present invention.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In FIGS. 1(a) and 1(b) there is schematically illustrated a linear quartz heat lamp 10 having a silica protective coating 11 according to the present invention. The lamp 10 includes a light transmissive envelope 12 which is typically a vitreous material such as quartz or fused silica. The envelope 12 includes a central portion defining a sealed chamber 14 and a press seal portion 22 at each end of the central portion. Hermetically sealed within the chamber 14 is a halogen fill typically comprising krypton and methyl bromide. A coiled tungsten filament 16 is horizontally disposed within the chamber 14 such that a longitudinal axis of the filament 16 is coincident with a longitudinal axis of the chamber 14. The filament 16 is supported within the chamber 14 by means of a plurality of tungsten or tantalum coiled wire filament supports 18. Each end of the filament 16 is welded or brazed to an end of an associated molybdenum foil seal 20. The foil seals 20 are hermetically sealed in the press seal portions 22 of the envelope 12. Lead wires 24 are attached to an end to the foil seals 20 opposite the filament 16 and outwardly extend from ends of the envelope 12.

A diffuse reflective coating 26, such as a boron nitride coating, is disposed on a portion of an exterior surface of the envelope 12. Walls of the envelope 12 typically reach temperatures in the range of about 800 to about 850 degrees centigrade (C) during operation of the lamp which is too high for metal coatings. Slightly less than half of the central portion of envelope 12 is covered by the diffuse reflective coating 26. The diffuse reflective coating 26 substantially reflects the visible and infrared radiation portions of the light emitted by the filament 16. As used in this specification and claims, "light" includes the visible and infrared portions of the spectrum. Using the diffuse reflective coating 26 on generally half or one side of the linear surface of the envelope 12 maximizes the infrared radiation or heat emitted in the direction of an item to be heated while minimizing heat emitted in the opposite direction.

The protective silica coating 11 of the illustrated embodiment is disposed on the diffuse reflective coating 26 and on a substantial portion of the envelope 12 to encapsulate and seal the diffuse reflective coating 26. It is noted that the protective silica coating 11 is only required to be adjacent a substantial portion of the diffuse reflective coating 26. However, the protective silica coating is preferably disposed on the entire exterior surface of the diffuse reflective coating 26, more preferably overlaps edges of the diffuse reflective coating 26 onto the lamp envelope 12, and most preferably is disposed on substantially the entire lamp envelope 12. As used in this specification and claims, "disposed on" contemplates that the coatings may be directly contacting or that there may be intermediate films or coatings such as, for example, a precoat or primer.

FIG. 2 schematically illustrates an arc lamp 30 having a silica protective coating 31 according to the present invention. The arc lamp 30 includes a light-transmissive vitreous quartz envelope 32 having a central portion defining an arc chamber and a press seal portion 34 at each end of the central portion. Hermetically sealed within the arc chamber is a pair of spaced apart electrodes and an arc sustaining fill comprising one or more metal halides and mercury. It will be noted that the arc lamp could alternatively be an electrodeless arc lamp. Each of the electrodes are welded or brazed to an end of an associated molybdenum foil seal 36. The foil seals 36 are hermetically sealed in the press seal portions 34 of the envelope 32. Lead wires 38 are attached to an end to the foil seals 36 opposite the electrodes and outwardly extend from ends of the envelope 32.

A diffuse reflective coating 40 is disposed on a portion of an exterior surface of the envelope 32. Both ends of the arc chamber, at the transition from the central portion to the press seal portions 34 of the envelope 32, are covered by the diffuse reflective coating 40. The diffuse reflective coating 40 is a coating, such as a boron nitride, aluminum oxide, or zirconium oxide coating, that substantially reflects visible and infrared radiation portions of the light emitted by the arc. The reflected radiation or heat minimizes or avoids condensation of the metal halide at the ends of the arc chamber during operation of the arc lamp 30. It is noted that the diffuse reflective coating 40 could be disposed on other portions of the envelope 32 to direct or reflect radiation emitted by the arc in a desired direction and/or to minimize radiation from being emitted in an undesired direction.

The protective silica coating 31 of the illustrated embodiment is disposed on the diffuse reflective coating 40 and on a substantial portion of the envelope 32 to encapsulate and seal the diffuse reflective coating 40. However, as noted above for the quartz heat lamp 10, the protective silica coating is only required to be adjacent to a substantial portion of the diffuse protective coating 40.

The protective silica coating is preferably a glassy silica which is derived from a coating precursor comprising a liquid dispersion of colloidal silica in a silicone. Silica is used here in a generic sense in that some silicates may also be present. Silicone is also used herein in its generic sense. Alternatively, the protective silica coatings 11, 31 can be any glassy, vitreous, or amorphous silica (SiO<sub>2</sub>) coating. The glassy silica provides a solid, abrasion resistant, hard, transparent, water and acetone impervious coating that can withstand temperatures up to about 1000 degrees C.

The protective silica coating has been made wherein the silicone of the coating precursor is a water-alcohol solution of the partial condensate of  $R(\text{Si}(\text{OH})_3)$  wherein R is an alkane, such as methyl trimethoxy silane. Examples of suitable silicones of this type, including some which are disclosed as containing colloidal silica, are disclosed, for example, in U.S. Patents 3,986,997, 4,275,118, 4,500,669 and 4,571,365, the disclosures of which are expressly incorporated herein by reference in their entirety. A suitable coating precursor is a silica hardcoat such as Silvue 313 Abrasion Resistant Coating obtained from SDC Coatings Inc., of Garden Grove, California. The Silvue 313 is a dispersion of colloidal silica in a solution of a partial condensate of  $R(\text{Si}(\text{OH})_3)$  wherein R is a methyl group. The dispersion contains 5% acetic acid, 13% n-butanol, 30% isopropanol, 1% methanol (all % by weight), and water. The total solids content of the colloidal silica and methyl trimethoxy silane ranges between 20-25% by weight.

The protective silica coating does not enhance or detract from the performance of the lamp because glassy silica has the same optical transmission characteristics as the quartz envelope. If the protective silica coating develops stress cracking or crazing, however, the performance of the lamp may be detracted. The cracks can cause diffuse scattering that reflects a portion of the heat back into the lamp. Additionally, the silica protective coating may not seal and protect the diffuse reflective coating if cracks are developed.

Stress cracking of the silica protective coating is prevented or minimized by material composition and processing, such as coating thickness, solvent concentrations and drying schedule. It is desirable to have a coating material with a coefficient of thermal expansion closely matching the coefficient of thermal expansion of the item to be coated. In this regard, the protective silica coating closely matches the quartz (fused silica) lamp envelope.

It is also desirable for the protective silica coating to have a thickness effective to both avoid stress cracking and protect the diffuse reflective coating from such things as abrasion, moisture and cleaning solvents. The thickness of the protective silica coating is typically in the range of about 0.1 to about 5 microns. The thickness is preferably in the range of about 0.5 to about 1.5 microns, however, to ease manufacturing of the coated lamps because the processing variables are more critical above or below this range. More preferably, the thickness of the protective silica coating is 1 micron.

To obtain the relatively thin coating, the coating precursor is diluted with solvents, such as butanol (butyl alcohol) and isopropanol (2-propanol). It is believed that other suitable alcohols can be used. A 1 micron thick protective silica coating has been made with a coating precursor solution of 70 cc of butanol and 70 cc of isopropanol added to 60 cc of the Silvue 313. It is believed that other solvent concentrations could be used with a suitable application method and drying schedule to obtain a coating with a suitable thickness to withstand cracking and crazing.

The coating precursor solution is preferably applied to the lamp by dipping the lamp into the solution so that the entire lamp or most of the lamp is covered to fully encapsulate and seal the diffuse reflective coating. The coating precursor solution can be applied to the lamp by other application methods such as, for example, spraying, pouring or brushing.

After the coating precursor solution has been applied to the lamp, it is dried at a low temperature to evaporate the solvents, that is, to drive off the hydrocarbons. The temperature must be high enough to drive off the hydrocarbons but low enough to prevent or minimize reaction of the silicone sol gel, and therefore, should be below 350 degrees C and preferably below 150 degrees C. If the coating precursor solution is heated to an elevated temperature too rapidly the hydrocarbons will be trapped and turn to graphite which results in a darkening or blackening of the coating. Preferably, the coating precursor solution is air dried for about 20 to 30 minutes and then oven dried at 150 degrees C for about 30 minutes.

After the coating precursor solution has been dried at a low temperature, the coating precursor is slowly heated in air to an elevated temperature to "cure" the coating, that is, to drive out or



pyrolyze the organics and densify the silica by cross linking the silicone sol gel to form glassy silica. The elevated temperature must be high enough to react the silicone sol gel, and therefore, should be above 350 degrees C. The coating precursor can be heated to the elevated temperature by baking the lamp in an oven, such as at 350 degrees C for about 30 minutes. When heating the lamp in the oven caution must be taken to ensure that components of the lamp, such as the molybdenum foil seals, are not damaged by the elevated temperature. Alternatively, and preferably, the coating precursor is heated to the elevated temperature by energizing the lamp. The quartz heat lamp, which typically has a temperature of about 600 to about 850 degrees C at the walls of the envelope during operation, is preferably energized for about 3 to about 5 minutes.

#### EXAMPLE 1

A coating precursor solution was made by adding 70 cc of butanol and 70 cc of isopropanol to 60 cc of Silvue 313. A GE QH2M T3/CL/HT/R 240 volt Quartz heat lamp having a boron nitride coating was dipped into the coating precursor solution and air dried at room temperature for about 20 to 30 minutes. The coated lamp was then placed in a laboratory oven at 150 degrees C for about 30 minutes to drive off the solvents. The lamp was then energized for about 3 to 5 minutes to drive off or pyrolyze the organic material and densify the silica to form glassy silica.

The coated lamp was then subjected to running water and was also rubbed with a damp cloth. The boron nitride coating was unharmed by the water or the rubbing. A similar lamp, but not coated with a protective silica coating, was also subjected to running water and rubbed with a damp cloth. The boron nitride coating was substantially removed from the lamp envelope.

#### EXAMPLE 2

A GE QH2M T3/CL/HT/R 240 volt Quartz heat lamp having a boron nitride coating was prepared in the same manner as described in Example 1. The coated lamp was then rubbed with an acetone damp cloth. The boron nitride coating was unharmed. A similar lamp, but not coated with a protective silica coating, was also rubbed with an acetone damp cloth. The boron nitride coating was substantially removed from this lamp envelope.

The invention has been described with reference to the preferred embodiments. Obviously, modifications and alterations will occur to others upon a reading and understanding of the specification. It is intended to include all such modifications and alterations insofar as they come within the scope of the appended claims or equivalents thereof.

1. An electric lamp comprising a vitreous light transmissive envelope having an exterior surface, a light source capable of generating light within said envelope, a diffuse reflective coating disposed on at least a portion of said exterior surface of said envelope for reflecting at least a portion of said light emitted by said source, and a protective silica coating disposed on said diffuse reflective coating.
2. The electric lamp according claim 1, wherein said protective silica coating is a glassy silica.
3. The electric lamp according to claim 1, wherein said diffuse reflective coating includes boron nitride.
4. The electric lamp according to claim 4, wherein said lamp is a quartz heat lamp, or an incandescent linear quartz heat lamp.
5. The electric lamp according to claim 3, wherein said lamp is an arc discharge lamp, said envelope has ends, and said diffuse reflective coating is disposed on the ends of said envelope.